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Courant Institute of
Mathematical Sciences

AEC Computing and Applied Mathematics Center

# Correlations Among Atomic Electrons

Meyer Katzper and Jerome Percus

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# CORRELATIONS AMONG ATOMIC ELECTRONS

by

Meyer Katzper and Jerome Percus

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# ABSTRACT

Methods for improving the calculation of energy values for atoms by accounting for the inter-particle correlation are presented. An approach using the projection of an intrinsic state wave function is first studied. A formalism for the use of intrinsic state density matrices is then presented and applied. The special properties of an oscillator based density matrix are investigated. As a result of these considerations a special N-body coordinate transformation is applied to a Slater determinant to form a correlated wave function and its related one and two body density matrices. A calculation is carried out to show the improvement resulting from this approach.

A harmonic atom approach with the use of unitary transformations to obtain a large class of one-body density matrices and guaranteed realizable two-body density matrices is then formulated. The formalism is tested in a calculation on Helium.

## 1. Introduction.

The most prevalent approach to many body problems is the Hartree-Fock method of approximating the solution to a given Hamiltonian H by an antisymmetrized product wave function $\psi$ composed of single particle functions $\phi_i$ which must be determined. Application of the variational principle

$$(1.1)\qquad \delta \int \psi^* H \psi \, d\tau = 0 \quad \text{subject to} \int \psi^* \psi \, d\tau = 1$$

gives rise to a set of non-linear integro-differential equations for the $\phi_i$ in which each particle moves in the average field of the other particles. For electrons in atoms, which we will be dealing with, the average coulomb interaction between one electron and the others is taken into account neglecting the correlation between the motion of the electrons. The best results obtained in this manner will be in error by an amount designated as the correlation energy $E_c$. The solution is usually obtained by an iteration procedure starting from a trial set of functions $\phi_i^0$. Any given trial solution of Hartree Fock form can be obtained from any other similar function by a product of one body unitary transformations U(i) where i represents the i-th coordinate. Symbolically,

$$(1.2)\qquad \psi^1 = U\psi^0 \quad \text{with} \quad U = \prod_{i=1}^{N} U(i) \; .$$

The trial set determines the potential which in turn determines the next set of wave functions. If the process converges it is continued until a self-consistent field is obtained.

The wave function obtained in this manner may give fairly good values for the energy but poor approximations to the true ground state wave function. The reason for the aforementioned is that in using the variational principle first order errors in the trial function produce only second order errors in the energy. To obtain a realistic wave function spatial correlation effects must be considered.

A number of methods have been employed to account for the correlation energy [1][*], [3]. One major approach is that of configuration interaction (CI) [2]. The true solution must satisfy the correlation cusp condition

(1.3a)
$$\left(\frac{1}{\psi}\frac{\partial\bar{\psi}}{\partial r_{ij}}\right)_{r_{ij}=0} = \frac{1}{2}$$

where $\bar{\psi}$ is averaged over the angle of $r_{ij}$. For any truncated configuration interaction function $\Phi_{CI}$

(1.3b)
$$\left(\frac{\partial\Phi_{CI}}{\partial r_{ij}}\right)_{r_{ij}=0} = 0 \ ,$$

---

[*] The numbers in [ ] are references.

so that no truncated $\Phi_{CI}$ can satisfy the correlation cusp condition. The present formulations will avoid this difficulty by involving a non-explicit and thus non-truncated configuration interaction. Completely arbitrary correlated trial wave functions are not in general use as in many particle systems they would be too complicated to use and too difficulty to integrate.

A class of approximate wave functions which includes correlation is given by Eq. (1.2) when $\psi_0$ is an interacting solution of some related problem of interacting particles. A still larger class is

$$\psi = \int F(\gamma)U_{\gamma}(1) \ldots U_{\gamma}(N)\psi_0 \, d\omega(\gamma) \tag{1.4}$$

a generalized intrinsic state model of the sort used in nuclear calculations. In fact this is the most general configuration interaction expansion and thus, in a sense, will include our approaches. To avoid the problem of multiple integrations the formalisms will be developed in terms of one and two body density matrices $\Gamma_1$ and $\Gamma_2$ which, however, present some difficulties in evaluation and the assuring of their legitimacy [4]. These questions will be examined.

## 2. Symmetry-Breaking Intrinsic States.

Stationary states have symmetry properties imposed by the nature of physical space which may conceal the nature of the specific system in question. A prototype of this is the spherically symmetric ground state of a rigid rotator, the rotator itself being quite asymmetric. Our point of view regarding this can be that all equally likely directions appear superimposed in the ground state, giving a projection onto the s-state. If the intrinsic anisotropic object is a particle system, even independent particles in an anisotropic potential, rotational averaging will produce new two particle correlations. As an example two electrons far apart have a tendency to be diametrically opposite each other with respect to the nucleus. The intrinsic state approach has been a valuable model technique in nuclear physics, where short range forces and close packing produce a somewhat rigid structure. More surprisingly, Auffray and Percus [5] have shown a rotational-intrinsic state to be very good for helium, by making a configuration expansion of their result.

The projective technique that is used with the intrinsic state to obtain spin and orbital angular momentum eigenfunctions for a rotationally invariant Hamiltonian is as follows. Let $\bar{x}_1$ denote space coordinates and $R_{\phi\theta\chi}$ a space rotation with Euler angles $\phi, \theta, \chi$ while $\bar{u}_i$ denotes spin coordinates and $S_{\phi\theta\chi}$ the corresponding spin rotation [6]. Define $\bar{x}_i' = R_{\phi\theta\chi}\bar{x}_i$,

$$(2.1) \qquad \bar{u}_i' = S_{\phi\theta\chi}\bar{u}_i , \qquad \psi' = R_{\phi\theta\chi} S_{\phi\theta\chi} \psi(\ldots\bar{x}_i,\bar{u}_i\ldots) \equiv \psi(\ldots\bar{x}_i',\bar{u}_i'\ldots) .$$

We now require

$$(2.2) \quad \psi_{JM}(\ldots x_i,u_i\ldots) = \iiint F(\phi,\theta,\chi)\psi'(\ldots\bar{x}_i,\bar{u}_i\ldots)\cdot \sin\theta \, d\theta \, d\phi \, d\chi .$$

That is, we must determine a weight function $F(\phi,\theta;\chi)$ which upon averaging over space and spin rotations will project out a wave function $\psi_{JM}$ of definite angular momentum J and its z component M. It is easily shown that in order to have

$$(2.3) \quad J_z\psi_{JM} = M\psi_{JM} \quad \text{and} \quad J^2\psi_{JM} = J(J+1)\psi_{JM}$$

$F(\phi,\theta,\chi)$ must satisfy precisely the equations for the rigid rotator whose solutions are well known [6]. In the simple two dimensional case $F(\phi,\theta,\chi)$ reduces to

$$(2.4) \qquad f(\theta) = \frac{1}{2\pi} e^{iM\theta} .$$

It is of interest to determine for what potential the projected wave function serves as a solution. Of course this will depend upon the nature of the initial many-body potential and upon the allowable state dependence. Sample calculations will therefore now be carried out using two dimensional cases.

Consider a two dimensional product function $u(x_1,y_1)v(x_2,y_2)$ which we distort to $u(\alpha_1x_1,\beta_1y_1)v(\alpha_2x_2,\beta_2y_2)$ which is not an angular momentum eigenfunction. Now project out an angular momentum eigenfunction

$$(2.5) \qquad \phi_j = P_j\psi = \frac{1}{2\pi}\int_0^{2\pi} d\phi_0 \; e^{-ij\phi_0} \; R(\phi_0)\psi(\ldots x_i,\ldots)$$

where $R(\phi_0)\psi(\ldots r_i\cos\phi_i\ldots) = \psi(\ldots r_i\cos(\phi_i+\phi_0)\ldots) = \bar{\psi}$. Taking a product wave function implies non-interaction between the particles. Distortion and projection gives rise to a non-product wave function with interaction between the particles.

$\nabla^2$ is invariant under rotation in the sense that if

$$(2.6) \quad \nabla^2 f(x,y) = g(x,y), \quad \nabla^2 R(\phi)f(x,y) = R(\phi_0)g(x,y)$$
$$= \nabla'^2 f(x',y') = g(x',y') \; .$$

So that if the differential equation u and v satisfy is known,

$$(2.7) \qquad \frac{\hbar^2}{2m}\nabla_1^2 R(\phi_0)\, uv = R(\phi_0)(V_u - E_u)\, uv \; .$$

The potential satisfied by $\phi_j$ now is

$$(2.8)\quad V''_j - E''_j = -\frac{T\phi_j}{\phi_j} = \frac{\frac{\hbar^2}{2m}\,\frac{1}{2\pi}\int_0^{2\pi} d\phi_0\; e^{-ij\phi_0}\;(\nabla_1^2 + \nabla_2^2)\;R(\phi_0)uv}{P_j\psi}$$

$$= -E_u - E_v + \frac{\frac{1}{2\pi}\int_0^{2\pi} d\phi_0 e^{-ij\phi_0} R(\phi_0)(V_u + V_v)uv}{P_j\psi} .$$

The last numerator, with its arguments written out, is

$$(2.9)\quad \frac{1}{2\pi}\int_0^{2\pi} d\phi_0\; e^{-ij\phi_0}\; R(\phi_0)\;(V_u(\alpha_1 x_1, \beta_1 y_1) +$$

$$+ V_v(\alpha_2 x_2, \beta_2 y_2))\; u(\alpha_1 x_1, \beta_1 y_1)\; v(\alpha_2 x_2, \beta_2 y_2) .$$

Equation (2.8) says

$$(2.10)\qquad T\phi + PVuv = (E_u + E_v)\phi \quad .$$

Therefore to satisfy a new Hamiltonian, H', we must have

$$(2.11)\qquad PVuv = (V' + C)Puv \; .$$

For a rotationally invariant potential V = V' we obtain the identity. Setting C = 0 would imply the unusual requirement that this energy level be the same for H and H'. Eq. (2.11) is generally not satisfied except in the highly artificial sense that

$$(2.12)\qquad V' = \frac{PVuv}{Puv} - C \; .$$

Possibly V can be considered a kernel for a sort of integral eigenvalue type equation.

We now apply this technique to a two dimensional two particle wave function solution of a noninteracting harmonic oscillator central field potential. The ground state for an unnormalized single particle, $u = \exp(-\alpha^2/2\ r_1^2)$, is distorted to

$$(2.13)\quad u = e^{-\frac{\alpha^2}{2} r_1^2} e^{-(q-1)\frac{\alpha^2}{2} y_1^2} = e^{-\frac{\alpha^2}{2} r_1^2 - (q-1)\frac{\alpha^2}{2} r_1^2 \sin^2\phi_1}$$

$$= e^{-(\frac{\alpha^2}{2} + \frac{1}{2}(q-1)\frac{\alpha^2}{2})r_1^2} e^{-\frac{1}{2}(q-1)\frac{\alpha^2}{2} r_1^2 \cos 2\phi_1}$$

$$\equiv e^{-B_1 r_1^2} e^{-A_1 r_1^2 \cos 2\phi_1} .$$

Similarly

$$(2.14)\qquad v = e^{-B_2 r_2^2} e^{-A_2 r_2^2 \cos 2\phi_2} .$$

The resulting projected wave function which is obtained is given in equation (2.18). To see the effect of this distortion and projection in modifying the Hamiltonian to the form which our new wave function will satisfy, rewrite the Schrodinger equation as

$$(2.15)\qquad V_D = \mathcal{E} + \frac{1}{2} k_1 \rho_1^2 + \frac{1}{2} k_2 \rho_2^2 + \frac{\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) Puv}{Puv} .$$

The result obtained is given in equation (2.19).

The same procedure is also carried out for a coulomb potential and the results are given in equations (2.20) and (2.21).

The following is a summary of results for the various cases based on the ground state wave functions:

1] Deformed two dimensional harmonic oscillator

$$(2.16)\quad \phi_\mu = P_\mu\, e^{-\frac{\alpha^2}{2}\rho^2}\, e^{-(q-1)\frac{\alpha^2 y^2}{2}}$$

$$= e^{-\frac{q+1}{4}\alpha^2\rho^2+i\mu\phi}\,(-1)^n\, I_n\!\left(\frac{q-1}{4}\alpha^2\rho^2\right)\ ,$$

where $\mu = 2n$. $I_n$ = modified Bessel function of first kind. Let $B = -(q+1)/4\ \alpha^2$, $A = q-1/4\ \alpha^2$.

$$(2.17)\quad V_n'' - E'' = \frac{h^2}{2m}\left[\ 4B(1+2n)+2(A^2+2B^2)\rho^2+\frac{n^2-\mu}{\rho^2}\ + \right.$$

$$\left. +\ \frac{I_{n+1}}{I_n}\,\{2A+n+8AB\lambda^2\}\right]\ .$$

2] Two non-interacting particles in deformed two dimensional harmonic oscillator potentials

$$(2.18)\quad \phi_\mu = P_\mu\, e^{-A_1\rho_1^2}\, e^{-A_1\rho_1^2\cos\, 2\phi_1}\, e^{-B_2\rho_2^2}\, e^{-A_2\rho_2^2\cos\, 2\phi_2}$$

$$= e^{-B_1\rho_1^2-B_2\rho_2^2}\, e^{-i\mu\Theta}\, I_n\!\left(\sqrt{A_1^2\rho_1+A_2^2+2A_1\rho_1^2A_2\rho_2^2\cos\, 2(\phi_2-\phi_1)}\ \right),$$

with

$$\Theta = \frac{1}{2}\tan^{-1}\frac{A_1\rho_1^2\sin\, 2\phi_1 + A_2\rho_2^2\sin\, 2\phi_2}{A_1\rho_1^2\cos\,\phi_1 + A_2\rho_2^2\cos\, 2\phi_2}$$

for u = 0.

$$(2.19)\quad V_0''-E_0'' = \hbar\omega_1 + \hbar\omega_2 - \frac{1}{2}k_1\rho_1^2 - \frac{1}{2}k_2\rho_2^2 + \frac{\hbar^2}{2m}[4A_1^2\rho_1^2 + 4A_2^2\rho_2^2$$

$$- \frac{4I_0'}{I_0}\left\{\frac{B_1(A_1^2\rho_1^4+A_1\rho_1^2A_2\rho_2^2\cos 2(\phi_2-\phi_1)+B_2(A_2^2\rho_2^4+A_1\rho_1^2A_2\rho_2^2\cos 2(\phi_2-\phi_1))}{\sqrt{A_1^2\rho_1^4+A_2^2\rho_2^4+2A_1\rho_1^2A_2\rho_2^2\cos 2(\phi_2-\phi_1)}}\right\}$$

3] Two non-interacting particles in a deformed hydrogenic potential.

$$(2.20)\quad \phi_\mu = P_\mu\, e^{-a_1\rho_1+b_1y_1}\, e^{-a_2\rho_2-b_2y_2}$$

$$= e^{-a_1\rho_1-a_2\rho_2}\, e^{-i\mu\textcircled{\scriptsize H}}(-1)^\mu\, \cdot$$

$$\cdot\, I_\mu\left(\sqrt{b_1^2\rho_1^2 + b_2^2\rho_2^2 - 2b_1\rho_1b_2\rho_2\cos(\phi_2-\phi_1)}\right)\ ;$$

$$\textcircled{\scriptsize H} = \text{cotan}^{-1}\frac{b_1\rho_1\sin\phi_1 - b_2\rho_2\sin\phi_2}{b_1\rho_1\cos\phi_1 - b_2\rho_2\cos\phi_2}\ ;$$

for u = 0.

$$(2.21)\quad V_0''-E_0'' = \frac{\hbar^2}{2m}[a_1^2 - \frac{a_1}{\rho_1} + a_2^2 - \frac{a_2}{\rho_2} + b_1^2 + b_2^2$$

$$- \frac{I_0'}{I_0}\left\{\frac{a_1(b_1^2\rho_1-b_1b_2\rho_2\cos\phi_2-\phi_1) + a_2(b_2^2\rho_2-b_1b_2\rho_1\cos\phi_2-\phi_1)}{\sqrt{b_1^2\rho_1^2+b_2^2\rho_2^2-2b_1\rho_1b_2\rho_2\cos(\phi_2-\phi_1)}}\right\}.$$

We note that this procedure gives rise to a rather odd interaction term in the form of a quotient of bessel functions. It appears that by insisting on a pure coordinate potential we have an intense state dependence and very complicated potentials.

If we allow momentum dependence and dependence on energy of state, a systematic development of an effective interaction is possible. We can write the projection of highest symmetry generally as an average over a group of unitary transformations

$$P = \int U_\gamma \, d\omega(\gamma) \tag{2.22}$$

where $U_\gamma = U_\gamma(1) \ldots U_\gamma(N)$, $U_\gamma U_{\gamma'} = U_{\gamma \cdot \gamma'}$, $\int d\omega(\gamma) = 1$, and $d\omega(\gamma \cdot \gamma') = d\omega(\gamma' \cdot \gamma) = d\omega(\gamma)$ for fixed $\gamma'$.

For example for two dimensional rotations

$$U_\theta = e^{\frac{i}{\hbar} \theta L_z} , \quad d\omega(\theta) = \frac{d\theta}{2\pi} . \tag{2.23}$$

Suppose we have an anisotropic Hamiltonian $H = T + \Delta$ such that $\Delta$ is the pure "anisotropic part" of H. In this case

$$\int U_\gamma \Delta \, U_\gamma^{-1} \, d\omega(\gamma) = 0 \tag{2.24}$$

as well as $[T,P] = 0$ , which may be realized by choosing $T = \int U_\gamma H U_\gamma^{-1} d\omega(\gamma)$.

Suppose further that $H\phi = E\phi$, and define

$$\psi = P\phi, \quad \psi' = P'\phi , \qquad \text{where } P' = 1-P . \tag{2.25}$$

Thus

(2.26) $$\begin{bmatrix} \Delta_1+T & \Delta_2 \\ \Delta_2^+ & \Delta_3+T \end{bmatrix} \begin{bmatrix} \psi \\ \psi' \end{bmatrix} = E \begin{bmatrix} \psi \\ \psi' \end{bmatrix}$$

so that

(2.27) $$\psi' = (E-T-\Delta_3)^{-1}\,\Delta_2^+\psi ,$$

and

$$(\Delta_1+\Delta_2[E-T-\Delta_3]^{-1}\Delta_2^+)\psi = (E-T)\psi .$$

Hence

(2.28) $$\bar{H}\psi = E\psi$$

where

$$\bar{H} = T + \Delta_1 + \Delta_2(E-T-\Delta_3)^{-1}\Delta_2^+ ,$$

and we can write

(2.29) $$H\psi \equiv \begin{pmatrix} \bar{H} & 0 \\ 0 & \Delta_3+T \end{pmatrix} \begin{pmatrix} \psi \\ 0 \end{pmatrix} = E \begin{pmatrix} \psi \\ 0 \end{pmatrix} .$$

Now

(2.30) $$P = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$$

so that

(2.31) $$\Delta_1 = P\Delta P, \quad \Delta_2 = P\Delta P', \quad \Delta_2^+ = P'\Delta P, \quad \Delta_3 = P'\Delta P' ,$$

and

(2.32) $$H = P(T + \Delta + \Delta P'[E-T-P'\Delta P')^{-1}P'\Delta)P + P'(T+\Delta)P'$$

or finally

$$(2.33)\quad H = T + (P\Delta P + P'\Delta P') + P\Delta P'(E-T-P'\Delta P')^{-1}P'\Delta P \ .$$

We can retain at most two body terms by replacing the reciprocal operator by its expectation

$$(2.34)\quad \frac{1}{\varepsilon} \equiv \langle\phi \mid P'(E-T-P'\Delta P')^{-1}P' \mid \phi\rangle \,/\, \langle\phi|P'|\phi\rangle \ .$$

Then

$$(2.35)\qquad H \sim T + (P\Delta P + P'\Delta P') + \frac{1}{\varepsilon}\, P\Delta P'\Delta P \ .$$

As a typical evaluation, note that

$$(2.36)\qquad \Delta \equiv \sum \Delta(i) \ , \qquad U_\gamma\psi = \psi \ ,$$

so $P\Delta P\Delta P$ can be replaced by

$$(2.37)\qquad P\Delta P\Delta = \int \sum U_\gamma \Delta(i) U_{\gamma'} \Delta(j)\; d\omega(\gamma)\; d\omega(\gamma') \ ,$$

which gives

$$(2.38)\quad \int \sum (U_\gamma \Delta(i) U_\gamma^+)(U_{\gamma'} \Delta(j) U_{\gamma'}^+)\; d\omega(\gamma)\; d\omega(\gamma')$$

$$= \int \sum (U_\gamma(i)\Delta(i)U_\gamma^+(i))(U_{\gamma'}(j)\Delta(j)U_{\gamma'}(j)\; d\omega(\gamma)\; d\omega(\gamma') .$$

Hence defining

$$(2.39)\quad \Delta_\gamma(i) \equiv U_\gamma(i)\Delta(i)U_\gamma^+(i) \ , \qquad [A_\gamma] \equiv \int A_\gamma\; d\omega(\gamma) \ ,$$

we have

$$(2.40)\ H \sim T + \sum [\Delta_\gamma(i)] + \frac{1}{\varepsilon}\sum_{i,j} ([\Delta_\gamma(i)\Delta_\gamma(j)] - [\Delta_\gamma(i)][\Delta_\gamma(j)] .$$

In particular since we have defined $\Delta$ such that $[\Delta_\gamma(i)] = 0$, then

$$(2.41) \qquad H \sim T + \frac{1}{\varepsilon} \sum_{i,j} [\Delta_\gamma(i)\Delta_\gamma(j)] \; .$$

As an example in the case of two dimensional space rotations with $\Delta$ only coordinate-dependent,

$$(2.42) \quad \Delta_\theta(i) = e^{\frac{i}{\hbar}\theta L_z} \Delta(\rho_i,\theta_i)\, e^{-\frac{i}{\hbar}\theta L_z} = \Delta(\rho_i,\theta_i+\theta)$$

so that

$$(2.43) \quad [\Delta_\gamma(i)\Delta_\gamma(j)] = \frac{1}{2\pi}\int \Delta(\rho_i,\theta_i+\theta)\; \Delta(\rho_j,\theta_j+\theta)\; d\theta$$

$$= \sum \Delta_n(\rho_i)\; \Delta_{-n}(\rho_j)\; e^{in(\theta_i-\theta_j)}$$

where $\Delta_n$ is the Fourier component of $\Delta$, and this is the two body interaction which is effective. For three dimensional space rotations very similar considerations hold, while the inclusion of spin rotations raises to two the rank of the coefficient of the Fourier terms, which is a very helpful generalization.

## 3. Intrinsic State Density Matrices.

When the intrinsic state is used as a variational ansatz, it introduces extra integrations to those already needed to compute the many-body averages used to determine expectation values. Griffin and Wheeler [9] use the intrinsic state trial wave function

$$(3.1) \quad \psi(x) = \int \phi(x;\beta)\ f(\beta)\ d\beta\ , \quad \psi^*(x) = \int \phi^*(x;\alpha)\ f(\alpha)\ d\alpha$$

with $f(\alpha)$ to be determined in the variational principle for energy (Eq. (1.1)), where the Hamiltonian contains particle coordinates only. In this case all quantities dependent on coordinates are known and the integrations over these variables can, in theory, be performed. Only integrations over $\alpha$ and $\beta$ will remain i.e.

$$(3.2) \qquad E = \frac{\int \psi^*(x)\ H\ \psi(x)\ (dx)}{\int \psi^*(x)\ \psi(x)\ (dx)}$$

$$= \int f^*(\alpha)\ K(\alpha,\beta)\ f(\beta)\ d\alpha\ d\beta \Big/ \int f^*(\alpha)\ I(\alpha,\beta)\ f(\beta) d\alpha\ d\beta .$$

Here the "overlap integral" I and the "energy kernel" K are abbreviations for the expressions

$$(3.3) \quad \begin{Bmatrix} I(\alpha,\beta) \\ K(\alpha,\beta) \end{Bmatrix} = \int \phi^*(x_1 \ldots x_N;\alpha) \begin{Bmatrix} 1 \\ H \end{Bmatrix} \phi(x_1 \ldots x_N;\beta)(dx).$$

Now f is varied to extremize (3.2). In this manner, an integral equation is obtained

$$(3.4) \qquad \int [K(\alpha,\beta) - I(\alpha,\beta)E]\, f(\beta)\, d\beta = 0 \ .$$

This equation as it stands is very difficult to deal with. Griffin and Wheeler [9] present arguments that for N large and $\psi$ well represented by a Slater determinant the overlap integral $I(\alpha,\beta)$ can be considered sharply peaked. They then approximate I by

$$(3.5) \qquad I(\alpha,\beta) = e^{-[s(\beta-\alpha)^2]} \ ,$$

and represent the ratio of the kernels K/I by a simple quadratic function of $\beta$ and $\alpha$

$$(3.6) \ K(\alpha,\beta) = \left\{ E_g + \frac{\hbar^2}{2\mathfrak{M}}[2s-4s^2(\beta-\alpha)^2] + \frac{1}{2}\mathfrak{M}\Omega^2\left(\frac{P+\alpha}{2}\right)^2 \right\} \cdot I(\alpha,\beta) .$$

Their approach thus makes only very limited use of the generality of Eq. (3.1).

The use of intrinsic state wave functions will here be approached from the point of view of intrinsic state density matrices. The required one and two body density matrices for the intrinsic state are to be found in terms of a basic independent particle one body density matrix in a fashion appropriate to large N and with a readily obtainable correction series. Generalizing to a projection onto other than the identity representation of a symmetry group, we want to determine the expectations associated with the N particle state

$$(3.7) \quad \psi(1\ldots N) = \sqrt{n} \int d\omega(\gamma)\ F(\gamma) \prod_{\ell=1}^{N} U_\gamma(\ell)(N!)^{-1/2} \operatorname{Det} u_k(\ell),$$

where $u_k(\ell)$ are single particle orbitals. The N body density matrix $\psi\psi^*$ is thus

$$(3.8) \quad \Gamma(1\ldots N|1'\ldots N') = \frac{n}{N!} \iint F(\gamma)\ F^*(\gamma')\operatorname{Det} U_\gamma(i)u_k(i)\cdot$$

$$\cdot(\operatorname{Det} U_\gamma(\ell)u_k(\ell))^*\ d\omega(\gamma)\ d\omega(\gamma')\ .$$

For a general N body wave function $\phi(1\ldots N)$ the associated first order density matrix is defined as

$$(3.9) \quad \Gamma\ (1|1') = N \int \phi(1,2,\ldots,N)\ \phi^*(1',2,\ldots,N)\ (dX_1)$$

where $(dX_1)$ means the integration is taken over all variables except 1 and 1', $(dX_{12})$ would omit 1,1',2,2', etc. The second order density matrix is defined as

$$(3.10) \quad \Gamma(1,2|1'2') =$$

$$\frac{N(N-1)}{2} \int \phi(1,2,3,\ldots,N)\ \phi^*(1',2',3,\ldots,N)\ (dX_{12})\ .$$

In our case let us consider our first order density matrix and expand the determinant by the 1,1' row and column obtaining

$$(3.11)\quad \Gamma(1|1') = \frac{n}{(N-1)!}\int\cdots\int F(\gamma)\, F^*(\gamma') \sum_{p,q} U_\gamma(1) u_p(1) \cdot$$

$$\cdot (U_{\gamma'}(1')u_q(1'))^* \operatorname{Det}_{\substack{\alpha\neq p\\ \beta\neq q}}\Big( \sum_{i\neq 1} U_\gamma(i)u_\alpha(i)(U_{\gamma'}(i)u_\beta(i))^*\Big)$$

$$\cdot (dX_1)\; d\omega(\gamma)\; d\omega(\gamma')$$

$$= n \iint F(\gamma)F^*(\gamma')U_\gamma(1)U^*_{\gamma'}(1') \sum_{p,q} u_p(1)u^*_q(1')Q_{pq}(\gamma',\gamma)$$

$$\cdot d\omega(\gamma)\; d\omega(\gamma')\ ,$$

where

$$(3.12)\quad Q_{pq}(\gamma',\gamma) = \operatorname{Det}_{\substack{\alpha\neq p\\ \beta\neq q}}\Big( \int U_\gamma(2)u_\alpha(2)(U_{\gamma'}(2)u_\beta(2))^*\, d2$$

Let

$$(3.13)\quad A_{rs} = \int u^*_s(1)\; U^*_{\gamma'}(1)\; U_\gamma(1)\; u_2(1)\; d1 = \langle u_s | U^*_{\gamma'} U_\gamma | u_r \rangle$$

and note that

$$(3.14)\quad Q_{pq}(\gamma'\gamma) = \text{cofactor } (A_{pq}) = A^{-1}_{qp} \det A = A^{-1}_{qp} e^{\operatorname{Tr} \ln A} .$$

To evaluate the density matrix we now make the approximation valid for large N, that the N x N submatrix of $\langle u_s | U^*_{\gamma'} U_\gamma | u_r\rangle$ is unitary as well. Hence

$$(3.15)\quad \Gamma(1|1') = n \iint F(\gamma)F^*(\gamma')\; e^{\operatorname{Tr}_N \ln U^*_{\gamma'} U_\gamma}\; U_\gamma(1)U^*_{\gamma'}(1')$$

$$\cdot \int \sum_p u_p(1)u^*_p(2)U^*_\gamma(2) \sum_q U_{\gamma'}(2)u_q(2)u^*_q(1')\; d2\; d\omega(\gamma)d\omega(\gamma') =$$

$$= n \iint F(\gamma)F^*(\gamma') \, e^{\mathrm{Tr}_N \ln U^*_\gamma, U_\gamma} \, U_\gamma(1) \, U^*_{\gamma'}(1')$$

$$\cdot \int \Gamma_0(1|2) \, U^*_\gamma(2) \, U_{\gamma'}(2) \, \Gamma_0(2|1') d2 \, d\omega(\gamma) \, d\omega(\gamma'),$$

where

$$\Gamma_0(1|1') = \sum_{r=1}^{N} u_r(1)u^*_r(1') \tag{3.16}$$

is the one body density matrix of the original wave function. In other words, we conclude that, in operator form

$$\Gamma_1 = n \, \bar{\Gamma}_1 \, \bar{\Gamma}^*_1 \tag{3.17}$$

where

$$\bar{\Gamma}_1(1|2) = \int F(\gamma) \, e^{\mathrm{Tr}(\Gamma_0 \ln U_\gamma)} \, U_\gamma(1)\Gamma_0(1|2)U^*_\gamma(2) \, d\omega(\gamma) \tag{3.18a}$$

or in a slightly different notation

$$\langle 1|\bar{\Gamma}_1|2\rangle = \int F(\gamma) \, e^{\mathrm{Tr}(\Gamma_0 \ln U_\gamma)} \langle 1|U_\gamma \Gamma_0 U^*_\gamma|2\rangle \, d\omega(\gamma). \tag{3.18b}$$

For the two body density matrix, $\Gamma_2$, proceeding in the same way we have (in our second notation to save writing labels)

$$\langle 1\ 2|\Gamma_2|\ 1'2'\rangle = \frac{n}{2} \sum_{p_1,p_2,q_1,q_2} \iint F(\gamma) \, F^*(\gamma')e^{\mathrm{Tr}_N \ln U_\gamma} \tag{3.19}$$

$$e^{\mathrm{Tr}_N \ln U^*_{\gamma'}} \, U_\gamma(1)u_{p_1}(1) \, U_\gamma(2)u_{p_2}(2)(U_\gamma(1')u_{q_1}(1'))^*(U_\gamma(2')u_{q_2}(2'))^*$$

$$[\langle u_{p_1}|U^*_\gamma U_{\gamma'}|u_{q_1}\rangle \, \langle u_{p_2}|U^*_\gamma U_{\gamma'}|u_{q_2}\rangle \, -$$

$$-\langle u_{p_1}|U^*_\gamma U_{\gamma'}|u_{q_2}\rangle \, \langle u_{p_2}|U^*_\gamma U_{\gamma'}|u_{q_1}\rangle] \, d\omega(\gamma) \, d\omega(\gamma').$$

Again identifying $\Gamma_0$ we obtain

$$(3.20)\quad \langle 1\ 2|\ \Gamma_2|1'2'\rangle = \frac{n}{2}\iint (F(\gamma)e^{Tr_N \ln U_\gamma})(F(\gamma')e^{Tr_N \ln U_{\gamma'}})^*$$

$$[\langle 1|U_\gamma\Gamma_0U_\gamma^*|3\rangle\langle 3|U_{\gamma'}\Gamma_0U_{\gamma'}^*|1'\rangle\langle 2|U_\gamma\Gamma_0U_\gamma^*|3'\rangle\langle 3'|U_{\gamma'}\Gamma_0U_{\gamma'}^*|2'\rangle$$

$$-\langle 1|U_\gamma\Gamma_0U_\gamma^*|3\rangle\ \langle 3|U_{\gamma'}\Gamma_0U_{\gamma'}^*|2'\rangle\langle 2\ |U_\gamma\Gamma_0U_\gamma^*|3'\rangle$$

$$\langle 3'|U_{\gamma'}\Gamma_0U_{\gamma'}^*|1'\rangle]\ d\omega(\gamma)\ d\omega(\gamma')\ ,$$

or in operator form

$$(3.21)\qquad \Gamma_2 = n\ \bar{\Gamma}_2\ \bar{\Gamma}_2^*$$

where

$$(3.22)\ \langle 1\ 2|\ \bar{\Gamma}_2|1'2'\rangle = \frac{1}{\sqrt{2}}\int F(\gamma)\ e^{Tr(\Gamma_0 \ln U_\gamma)}.$$

$$\cdot[\langle 1|U_\gamma\Gamma_0U_\gamma^*|1'\rangle\langle 2|U_\gamma\Gamma_0U_\gamma^*|2'\rangle\ -$$

$$-\ \langle 1|U_\gamma\Gamma_0\ U_\gamma^*|2'\rangle\ \langle 2|U_\gamma\Gamma_0U_\gamma^*|1'\rangle]\ d\omega(\gamma)\ .$$

We thus have a formalism for dealing with any case where we have reason to believe that the states of a system may be given by projection of an intrinsic state. Given the one body density matrix for an intrinsic state we can determine the correlated one and two body density matrices for the projected state. We shall subsequently generalize this formalism to include an additional transformation and apply the results to atoms. Now we will consider the case of a periodically bounded particle along the x axis and perform a two dimensional rotational average to illustrate the effects obtained. Our single particle wave functions are

$$(3.23) \qquad \phi_k(x,y) = e^{ikx} \delta(y) \ ,$$

so that our original one body density matrix is

$$(3.24) \qquad \Gamma_0(1|2) = \sum_k \psi_k(x_1 y_1) \, \psi_k^*(x_2 y_2)$$

$$= \frac{\sin \frac{N}{2} (x_1 - x_2)}{\sin \frac{1}{2} (x_1 - x_2)} \, \delta(y_1) \, \delta(y_2)$$

for N odd.

Under rotation this becomes

$$(3.25) \qquad \frac{\sin \frac{N}{2} (x_1 \cos \theta + y_1 \sin \theta - x_2 \cos \theta - y_2 \mathrm{iin}\ \theta)}{\sin \frac{1}{2} (x_1 \cos \theta + y_1 \sin \theta\beta x_2 \cos \theta - y_2 \sin \theta)}$$

$$\delta(y_1 \cos \theta - x_1 \sin \theta) \, \delta(y_2 \cos \theta - x_2 \sin \theta)$$

which integrates to give

$$(3.26) \qquad \langle 1| \, \bar{\Gamma}_1 |2\rangle = \frac{\sin \frac{N}{2} (\rho_1 - \rho_2)}{\sin \frac{1}{2} (\rho_1 - \rho_2)} \, \frac{\delta(2\phi_1 - 2\phi_2)}{\rho_1 \rho_2}$$

an expression which is not normalizable but which shows the typical strong anisotropy of diametric correlation.

## 4. Oscillator Based Density Matrix.

There is one independent-particle model in which averaging out over a somewhat unusual broken symmetry has precisely the effect of introducing pair interactions. Proceeding in reverse order, one can turn on harmonic interactions between harmonically bound particles by the transformation of the Hamiltonian

$$H_0 = \sum \frac{p_i^2}{2m} + \frac{m\omega^2}{2} \sum x_i^2 \tag{4.1}$$

by shifting all the coordinates with respect to the center of mass

$$x_i \to x_i - \lambda \sum_j x_j \quad \text{and letting } K = (2\lambda - \lambda^2 N) m\omega^2, \tag{4.2}$$

to give

$$H = \sum_i \frac{p_i^2}{2m} + \frac{m\omega^2 - K}{2} \sum_i x_i^2 - \frac{K}{2} \sum_{i \neq j} x_i x_j \; . \tag{4.3}$$

In terms of center of mass and relative coordinates and momentum

$$\begin{aligned} p_i &= \bar{p}_i + \frac{p}{N^{1/2}} \, , & p &= \frac{1}{N^{1/2}} \sum p_i \, , \\ x_i &= \bar{x}_i + \frac{x}{N^{1/2}} \, , & x &= \frac{1}{N^{1/2}} \sum x_i \; . \end{aligned} \tag{4.4}$$

The relative part of $H_0$ under our transformation

$$H_{0\ \text{rel}} = \sum \frac{\bar{p}_i^2}{2m} + \frac{m\omega^2}{2} \sum \bar{x}_i^2 \tag{4.5}$$

is unchanged, but the center of mass part

$$(4.6) \qquad H_{O\ C.M} = \frac{p^2}{2m} + \frac{m\omega^2}{2} x^2$$

is transformed into

$$(4.7) \qquad H_{C\ M} = \frac{p^2}{2m} + \frac{m\omega^2 - NK}{2} x^2 .$$

Thus the corresponding wave functions are connected by the unitary transformation which takes

$$(4.8) \qquad \frac{1}{\omega} \left(\frac{p^2}{2m} + \frac{m\omega^2}{2} x^2\right)$$

into

$$\frac{1}{(\omega^2 - \frac{NK}{m})^{1/2}} \left(\frac{p^2}{2m} + \frac{m\omega^2 - NK}{2} x^2\right)$$

(where we have divided by frequency to identify spectra). Our transformation therefore takes

$$(4.9) \qquad P \quad \text{into} \quad \frac{1}{(1 - \frac{NK}{m\omega^2})^{1/4}} P$$

and

$$X \quad \text{into} \quad (1 - \frac{NK}{m\omega^2})^{1/4} X$$

so that a general function F goes to $UFU^*$ where

$$(4.10) \qquad U = :e^{-\frac{i}{\hbar}[1-(1-NK/m\omega^2)^{1/4}]X\cdot P}:$$

which can be written in the form

$$(4.11)\quad U = \frac{1}{\frac{2\pi}{\hbar}\left(1-\left(1-\frac{NK}{m\omega^2}\right)^{1/4}\right)} \cdot$$

$$\cdot \iint e^{i\hbar/(1-(1-NK/m\omega^2)^{1/4})s\cdot t}\, e^{is\cdot x}\, e^{it\cdot p}\, ds\, dt \ .$$

Hence setting $\lambda = 1-(1-NK/m\omega^2)^{1/4}$, we have

$$(4.12)\qquad U = \frac{1}{2\lambda}\,\frac{N\hbar}{\lambda} \iint e^{i\frac{N\hbar}{\lambda}s\cdot t} \prod_j \left(e^{is\cdot x_j}\, e^{it\cdot p_j}\right) ds\, dt \ .$$

The many-body center of mass-magnifying transformation U is thus an average of one-body unitary transformations, any of which destroys the x-p reciprocity symmetry (Born-Yukawa) of the Hamiltonian. According to our approximation method, the basic generating transformation is given by

$$\langle x|\bar{\Gamma}_1|y\rangle = \int e^{i\frac{N\hbar}{\lambda}s\cdot t} \sum e^{is\cdot x}\, u_n(x+\hbar t)\, u_n^*(y+\hbar t)\, e^{-is\cdot y}\, ds\, dt$$

and $\bar{\Gamma}_2$ is similarly obtained. In Section 5, we carry out a direct application of the many-body transformation on the N particle density matrix and obtain the expressions for the one and two body density matrices, to within our approximation, in terms of the uncorrelated density matrices. On the basis of these representations of $\Gamma_1$ and $\Gamma_2$ some properties of the density matrices are easily shown and application is made of the formalism.

We thus have an interaction producing transformation which we know is effective for harmonic oscillators. We still must obtain the basic $\Gamma_0$. Consider closed-shell atoms. To within a simple coordinate transformation, harmonic oscillator and Coulomb wave functions are quite similar. If $n_r$ denotes the radial quantum number, for the harmonic oscillator

$$(4.14) \quad \psi_{n_r \ell m} = \sqrt{2}\, \alpha^{\ell+3/2} \left( \frac{n_r!}{(n_r+\ell+\frac{1}{2})!} \right)^{1/2} x^{\ell}\, e^{-\frac{1}{2}\alpha^2 x^2} \cdot$$

$$\cdot\, L_{n_r}^{\ell+1/2}(\alpha^2 x^2)\, Y_{\ell}^{m}(\theta,\phi) \;,$$

and

$$E_{n_r \ell m} = (2n_r + \ell + \tfrac{3}{2})\, \hbar\, \omega$$

while for the Coulomb case,

$$(4.15) \quad \psi_{n_r \ell m} = \frac{k_0^{\ell+3/2}}{(n_r+\ell+1)^{\ell+3/2}}\, x^{\ell}\, e^{-\frac{1}{2}\left(\frac{k_0}{n_r+\ell+1}\right)x} \;.$$

$$\cdot\, L_{n_r}^{(2\ell+1)}\left( \frac{k_0}{n_r+\ell+1}\, x \right) Y_{\ell}^{m}(\theta,\phi) \;,$$

and

$$E_{n_r \ell m} = -\frac{k_0 \ell^2}{4(n_r+\ell+1)^2} \;;$$

but they can be made to correspond exactly under a one body unitary transformation. However the Coulomb level ordering with energy is not the same as that for the harmonic oscillator, so that transforming the relatively easy harmonic oscillator Fermi sphere $\Gamma_0$ is not sufficient.

Instead we note that for the Coulomb Fermi sphere, $n_r+\ell+1 \le n$. For harmonic oscillators this means that $E/\hbar\omega \le 2n-(\ell+1/2)$, or $L^2/\hbar^2 \le (2n- E/\hbar\omega)^2 - 1/4$. The annihilation and creation operators for a harmonic oscillator are

$$(4.16a) \quad a = \frac{1}{\sqrt{2\hbar m\omega}}\, p + i \sqrt{\frac{m\omega}{2\hbar}}\, x \;, \qquad b \equiv a^* = \frac{1}{\sqrt{2\hbar m\omega}} x - i \sqrt{\frac{m\omega}{2\hbar}}\, x$$

or

$$(4.16b) \quad p = \sqrt{\frac{\hbar m\omega}{2}}\,(a+b) \;, \qquad x = \sqrt{\frac{\hbar}{2m\omega}}\;\frac{a-b}{i}$$

and then

$$(4.16c) \quad \psi_n = \frac{1}{\sqrt{n}\;!}\, b^n\, \psi_0$$

for each dimension.

Now

$$(4.17a) \qquad L_z = x_1p_2 - x_2p_1 = \frac{\hbar}{i}(b_1a_2-b_2a_1)$$

so

$$(4.17b) \qquad L = \hbar/i \;\; \underline{b} \times \underline{a}$$

and

$$(4.17c) \qquad E = (\underline{b}\cdot\underline{a} + \tfrac{3}{2})\hbar\omega \;.$$

Further,

$$(4.18) \quad (b \times a)^2 + (b\cdot a)^2 = \,:(b\times a)^2:\, -2b\cdot a + \,:(b\cdot a)^2:\, + b\cdot a$$

$$= b^2a^2 - \underline{b}\cdot\underline{a}$$

so that the closed shell condition becomes

$$(4.19)\quad 0 \le \left(\frac{E}{\hbar\omega} - \frac{3}{2}\right)^2 + \left(2n - \frac{3}{2}\right)^2 - 2\left(2n - \frac{3}{2}\right)\left(\frac{E}{h\omega} - \frac{3}{2}\right) - \frac{1}{4} - \frac{L^2}{\hbar^2}$$

$$= b^2a^2 - \left(\frac{E}{\hbar\omega} - \frac{3}{2}\right) - (4n-3)\left(\frac{E}{\hbar\omega} - \frac{3}{2}\right) + 4n^2 - 6n + 2$$

$$= b^2a^2 - \left(\frac{E}{\hbar\omega} - \frac{3}{2}\right) 2(2n-1) + 4n^2 - 6n + 2 \ .$$

This yields a one body density matrix (with Z a unit step up at the origin) of

$$(4.20)\quad \Gamma_0 = NZ[b^2a^2 - 2(2n-1)(b \cdot a + \tfrac{3}{2}) + (2n+1)(2n-1)] \ ,$$

which of course can be used for annihilation-creation structures other than those of the oscillator.

When we apply the $\Gamma_1$ approximation method to a pair of oscillators, in Section 5, the result is found to be exact. This is not far from true for any set of independent oscillator states. The reason is that due to Eq. (4.16b) the unitary transformations required are very special. They are exponentials of linear combinations of annihilators and creators

$$(4.21)\qquad U_\gamma = e^{(\gamma \cdot a^* - \gamma^* \cdot a)}$$

with the property of having a closed form inverse on any N by N subspace without holes. By a subspace of orbitals without holes, we mean one taken into itself by a.

It then follows that for the states $p,q \leq N$,

$$(4.22)\quad \langle p|e^{\beta a^*} e^{\alpha a}|q\rangle = \sum_{\mu=1}^{\infty} \langle p|e^{\beta a^*}|\mu\rangle\langle\mu|e^{\alpha a}|q\rangle$$

$$= \sum_{\mu=1}^{N} \langle p|e^{\beta a^*}|\mu\rangle\langle\mu|e^{\alpha a}|q\rangle$$

while

$$(4.23a)\quad \sum_{\mu=1}^{N} \langle p|e^{-\alpha a}|\mu\rangle\langle\mu|e^{\alpha a}|q\rangle = \sum_{\mu=1}^{\infty} \langle p|e^{-\alpha a}|\mu\rangle\langle\mu|e^{\alpha a}|q\rangle$$

$$= \delta_{pq} ,$$

with its conjugate

$$(4.23b)\quad \sum_{\mu=1}^{N} \langle q|e^{\beta a^*}|\mu\rangle\langle\mu|e^{-\beta a^*}|p\rangle = \delta_{pq} .$$

Hence if

$$(4.24a)\qquad U_{pq} = \langle u_p|\ U\ |u_q\rangle$$

we have

$$(4.24b)\quad U_{pq} = e^{-\frac{1}{2}\gamma\cdot\gamma^*} \langle p|e^{\gamma a^*} e^{-\gamma^* a}|q\rangle$$

$$= e^{-\frac{1}{2}\gamma\cdot\gamma^*} \sum_{\mu=1}^{N} \langle p|e^{\gamma a^*}|\mu\rangle\langle\mu|e^{-\gamma^* a}|q\rangle$$

or

$$(U^{-1})_{qp} = e^{\frac{1}{2}\gamma\cdot\gamma^*} \sum_{\mu=1}^{N} \langle q|e^{\gamma^* a}|\mu\rangle\langle\mu|e^{-\gamma\cdot a^*}|p\rangle$$

while

$$(4.25)\quad \mathrm{Det}\, U = e^{-\frac{N}{2}\gamma\cdot\gamma^*}\ \mathrm{Det}\,\langle q|e^{\gamma\cdot a^*}|\mu\rangle\ \mathrm{Det}\,\langle\mu|e^{-\gamma^* a}|p\rangle$$

$$= e^{-\frac{N}{2}\gamma\cdot\gamma^*}\,.$$

Thus

$$(4.26)\quad \underset{\substack{\alpha\neq p\\ \beta\neq q}}{\mathrm{Det}}\langle u_\beta|U^*_{\gamma'}U_\gamma|u_\alpha\rangle = e^{-\frac{N-1}{2}(\gamma-\gamma')(\gamma-\gamma')^*}\,.$$

$$\cdot\ e^{\frac{N-1}{2}(\gamma'^*\gamma-\gamma'\cdot\gamma'')}\sum_{\mu=1}^{N}\langle q|e^{(\gamma-\gamma')^*\cdot a}|\mu\rangle\langle\mu|e^{-(\gamma-\gamma')\cdot a^*}|p\rangle.$$

In our approximation we require the replacement of

$$(4.27)\qquad (U_\gamma\Gamma_0 U^*_\gamma)(U_{\gamma'}\Gamma_0 U^*_{\gamma'})$$

by

$$e^{-\frac{N}{2}(\gamma\gamma^*+\gamma'\gamma'^*-2\gamma'^*\cdot\gamma)}\ U_\gamma\Gamma_0 U^*_\gamma(e^{\gamma a^*-\gamma'^* a}\,\Gamma_0\ e^{-\gamma a^*+\gamma'^* a})U_{\gamma'}\Gamma$$

with a similar direct modification for $\Gamma_2$.

## 5. Correlation through Transformation.

The many body transformation of Section 4 will here be used directly to introduce correlation and obtain the approximate oscillator based density matrix. The coordinate dependence of the diagonal elements will be shown to be exact. For the case of two particles in a harmonic oscillator potential our density matrix will give the exact result for the harmonic oscillator interaction. In the noninteracting N particle density matrix, formed by Slater determinants, displace each coordinate by a fraction of the center of mass of the system. Let

$$(5.1)\quad \bar{x}' = \tilde{x} + \bar{x}_1 \;, \quad \tilde{x} = \sum_{i=2}^{N} \bar{x}_i \;, \quad \bar{y}' = \tilde{y} + \bar{y}_1 , \quad \tilde{y} = \sum_{i=2}^{N} \bar{y}_i .$$

Our determinants will be specified symbolically by giving one of their elements.

$$(5.2)\quad \langle \ldots x_i \ldots | \Gamma^{(N)} | \ldots y_i \ldots \rangle =$$

$$= n \operatorname{Det} u_p(x_i + \lambda \bar{x}') \operatorname{Det} u_p^*(y_i + \lambda \bar{y}') .$$

Within a normalization factor n which we omit in the following,

$$(5.3)\quad \langle x | \Gamma^{(N)}(1) | y \rangle = \operatorname{Tr}_{2\ldots N} \langle x | \Gamma^{(N)} | y \rangle$$

$$= \int dx_2 \ldots dx_N \iint e^{-is(R-\tilde{x})} \quad .$$

$$\cdot \operatorname{Det} u_p(x_i + \lambda R + \lambda x_1) \operatorname{Det} u_p^*(x_j + \lambda R + \lambda y_1) \, dR \, ds;$$

expanding each determinant by minors this is (letting $x_1 = x$, $y_1 = y$):

$$= \iint dR \, ds \, e^{-is\cdot R} \sum_{r,s} u_r(x + \lambda R + \lambda x) \, u_s^*(y + \lambda R + \lambda y) \cdot$$

$$\cdot \, Q'_{rs}[s, R+y, R+x] \, ,$$

where $Q'_{rs}$ = cofactor $(\alpha'_{rs})$.

$$(5.4) \quad \alpha'_{qp} = \int e^{is\cdot x_i} u_p^*(x_i + \lambda R + \lambda y) \, u_q(x_i + \lambda R + \lambda x) \, dx_i \; .$$

In these $\alpha'_{qp}$, let $x'_i = x_i + \lambda R$, so $\alpha'_{qp} = e^{-i\lambda s\cdot R} \alpha_{qp}$ , with

$$(5.5) \quad \alpha_{qp} = \int u_p^*(x_i + \lambda y) \, e^{is\cdot x_i} \, u_q(x_i + \lambda x) \, dx_i \; ,$$

and $Q_{rs}$ = cofactor $(\alpha_{rs})$.

$$(5.6) \quad \langle x | \Gamma^{(N)}(1) | y \rangle = \iint ds \, dR \, e^{-is\cdot R[1+(N-1)\lambda]}$$

$$\cdot \sum_{r,s} u_r(x[1+\lambda]+\lambda R) \, u_s^*(y[1+\lambda]+\lambda R) \, Q_{rs}[s,y,x].$$

This expression is exact and derived from a known N particle wave function with we have reduced to a double (3 dimensional) integral of products of single integrals. We can simplify this further (-- with respect to getting a tractable expression) by the following procedure. We note that

$Q_{rs} = \alpha^{-1}_{sr} \det \alpha$, but evaluation of $\alpha^{-1}$ is a laborious undertaking at best. We may write

$$(5.7) \qquad \alpha_{qp} = \langle u_p | e^{-\frac{i}{h}\lambda yp} \, e^{is\cdot x_1} \, e^{\frac{i}{h}\lambda xp} | u_q \rangle .$$

When higher order commutation brackets give zero, we have the operator equation

$$(5.8) \qquad e^{\alpha(A+B)} = e^{\alpha A} \, e^{\alpha B} \, e^{-\frac{1}{2}\alpha^2 [A,B]} .$$

We may therefore express the operator $\alpha$ as

$$(5.9) \quad \alpha = e^{-\frac{i}{h}\lambda yp} \, e^{is\cdot x_1} \, e^{\frac{i}{h}\lambda xp}$$

$$= e^{-i\frac{\lambda s}{2}(x+y)} \, e^{(-\frac{i}{h}\lambda yp + isx_1 + \frac{i}{h}\lambda xp)} .$$

So that for a complete set ($\infty$ matrix) the inverse element is immediately known

$$(5.10) \qquad \underset{\infty}{\alpha^{-1}_{qp}} = \int u_p^*(x_1 + \lambda x) e^{-is\cdot x_1} u_q(x_1 + \lambda y) \, dx_1 .$$

We will also use the relationship

$$(5.11) \qquad \operatorname{Det} A = e^{\operatorname{Tr} \ln A} = e^{\sum_s (\ln A)_{ss}} .$$

We will now use these relationships to approximate $Q_{rs}$ by the inverse of the $\infty$ matrix multiplying the N by N determinant.

$$(5.12)\quad Q_{rs} \cong \langle u_r | e^{-\frac{i}{\hbar}\lambda xp} e^{-is\cdot x_i} e^{\frac{i}{\hbar}\lambda yp} | u_s \rangle \cdot$$

$$\cdot \exp\left\{ -i\,\frac{\lambda}{2}\,Ns(x+y) + \sum_{i=1}^{N} \left(-\frac{i}{\hbar}\lambda yp + isx_i + \frac{i}{\hbar}\lambda xp\right)\right\}$$

For states of definite parity the sum which has linear arguments in x and ∂/∂x vanishes. To the above approximation we now have:

$$(5.13)\quad \langle x | \Gamma^{(N)}(1) | y \rangle = \iint e^{-is\cdot R[1+(N-1)\lambda]}\, e^{-i\frac{\lambda Ns}{2}(x+y)}$$

$$\sum_{r,s}^{N,N} u_r(x[1+\lambda]+\lambda R)\,u_s^*(y[1+\lambda]+\lambda R)\cdot \int dx_1\; u_r^*(x_1+\lambda x)\cdot$$

$$\cdot e^{-is\cdot x_1}\; u_s(x_1+\lambda y)\; ds\; dR\ .$$

Taking $\int ds$ and then $\int dx_1$,

$$= \int dR \sum_{r,s}^{N,N} u_r(x[1+\lambda]+\lambda R)\,u_r^*(-R[1+(N-1)\lambda] - \frac{\lambda N}{2}(x+y) + \lambda x)$$

$$u_s(-R[1+(N-1)\lambda] - \frac{\lambda N}{2}(x+y) + \lambda y)\; u_s^*(y[1+\lambda]+\lambda R)$$

$$(5.14)\quad = \int dR\; \Gamma(x+\lambda[x+R], -R+\lambda[x+R] - \frac{N\lambda}{2}(x+y+2R))\cdot$$

$$\cdot \Gamma(-R+\lambda(y+R) - \frac{N\lambda}{2}(x+y+2R),\; y+\lambda[y+R])\ .$$

For $\lambda = 0$, we obtain

$$(5.15)\qquad \Gamma(x,y) = \langle x | \Gamma^{(N)}(1) | y \rangle$$

as required for a legitimate density matrix of noninteracting particles (i.e. $\int \Gamma(x,R)\Gamma(R,y)\,dR = \Gamma(x,y)$). The second order density matrix is (without the normalization factor n)

$$(5.16)\quad \langle x_1x_2|\Gamma^{(N)}(2)|y_1y_2\rangle = \mathrm{Tr}_{3\ldots N}\langle\ldots x_i\ldots|\Gamma^{(N)}|\ldots y_i\ldots\rangle$$

$$= \int dx_3 \ldots dx_N \iint e^{-is\cdot(R-\bar{x}_2)}\,dR\,ds\,\cdot$$

$$\cdot\ \mathrm{Det}\,u_p(x_i+\lambda R+\lambda(x_1+x_2))\ \mathrm{Det}\,u_p^*(x_j+\lambda R+\lambda(y_1+y_2))\ ,$$

with $\bar{x}_2 = \sum_{i=3}^{N} x_i$. We now use a "double minor expansion" on each determinant to separate nonintegrated terms. Analogously to $Q_{rs}$

$$(5.17a)\quad Q_{\substack{rs\\tu}} = \text{cofactor}\,(\alpha_{rs}\alpha_{tu}) = (\alpha^{-1}_{sr}\alpha^{-1}_{ut} - \alpha^{-1}_{ur}\alpha^{-1}_{st})\ \det\alpha\ ,$$

which vanishes for $r = t$ or $s = u$, with

$$(5.17b)\quad \alpha_{qp} = \int u_p^*(x_i+\lambda[y_1+y_2])\,e^{is\cdot x_i}\,u_q(x_i+\lambda[x_1+x_2])\,dx_i\ .$$

Now (5.16) is

$$(5.18)\qquad \iint ds\,dR\ e^{-is\cdot R[1+(N-2)\lambda]}\,\cdot$$

$$\cdot \sum_{r,s,t,u}^{N} u_r(x_1[1+\lambda]+\lambda[R+x_2])\,u_s^*(y_1[1+\lambda]+\lambda[R+y_2])\,\cdot$$

$$\cdot\ u_t(x_2[1+\lambda]+\lambda[R+x_1])\,u_u^*(y_2[1+\lambda]+\lambda[R+y_1])\,\cdot$$

$$\cdot\ Q_{\substack{rs\\tu}}(s,y_1+y_2,\ x_1+x_2)\ .$$

We now follow the same procedure as for $\Gamma(1)$ so for states of definite parity we obtain

$$(5.19)\quad Q_{\substack{rs\\ tu}} \cong e^{-i\frac{\lambda N}{2} s\cdot(X)}\Big[\int u_r^*(x_i+\lambda\bar{x})e^{-is\cdot x_i} u_s(x_i+\lambda\bar{y})dx_i \cdot$$

$$\cdot\int u_t^*(x_j+\lambda\bar{x})\, e^{-is\cdot x_j}\, u_u(x_j+\lambda\bar{y})\, dx_j -$$

$$-\int u_r^*(x_i+\lambda\bar{x})\, e^{-is\cdot x_i}\, u_u(x_i+\lambda\bar{y})\, dx_i \cdot$$

$$\cdot\int u_t^*(x_j+\lambda\bar{x})\, e^{-is\cdot x_j}\, u_s(x_j+\lambda\bar{y})\, dx_j\Big]\ ,$$

with $\bar{x} = x_1+x_2$, $\bar{y} = y_1+y_2$, $X = \bar{x}+\bar{y}$; $\alpha^{-1}_{\substack{sr\\ \infty}}$ has been used here. Put this in equation (5.18), and we obtain $\delta(x_i+x_j+R(1+(N-2)\lambda]+ +(\lambda N/2)X)$. Let $\mathcal{L}(\lambda,N) = \mathcal{L} \equiv 1+(N-2)\lambda$. We obtain

$$(5.20)\quad \langle x_1x_2|\Gamma^{(N)}(2)|y_1y_2\rangle = \int dR\int d\tilde{x}\,\Big\{\Gamma(x_1+\lambda[R+\bar{x}],\tilde{x}+\lambda\bar{x})\ .$$

$$\cdot\ \Gamma(x_2+\lambda[R+\bar{x}],-\tilde{x}-R\mathcal{L}-\frac{\lambda N}{2}X+\lambda\bar{x})\cdot[\Gamma(\tilde{x}+\lambda\bar{y},y_1+\lambda[R+\bar{y}])\cdot$$

$$\cdot\ \Gamma(-\tilde{x}-R\mathcal{L}-\frac{\lambda N}{2}X+\lambda\bar{y},y_2+\lambda[R+y])-\Gamma(\tilde{x}+\lambda\bar{y},y_2+\lambda[R+\bar{y}])\cdot$$

$$\cdot\ \Gamma(-\tilde{x}-R\mathcal{L}-\frac{\lambda N}{2}X+\lambda\bar{y},\ y_1+\lambda[R+\bar{y}])]\Big\}\ .$$

The correctness of the functional form obtained for diagonal matrix elements by our formalism is proven as follows:

For $x = y$, let $x_i' = x_i + \lambda x$, so that

$$(5.21)\quad \alpha_{qp} = e^{-is\cdot\lambda x}\int e^{is\cdot x_i'}\, u_p^*(x_i')\, u_q(x_i)\, dx_i'$$

$$\equiv e^{-is\cdot\lambda x}\, c_{qp}(s)\ .$$

Let $\bar{Q}_{rs}(s)$ = cofactor $(c_{rs})$; so that now

$$(5.22)\ \langle x|\Gamma^{(N)}(1)|x\rangle = \iint dR\, ds\, e^{-is\cdot R[1+(N-1)\lambda]}$$

$$\cdot\ e^{-i\bar{s}\cdot\bar{x}\ \lambda(N-1)} \sum_{r,s} u_r(x[1+\lambda]+\lambda R)\, u_s^*(x[1+\lambda]+\lambda R)\, \bar{Q}_{rs}(c);$$

$$(5.23)\quad \underset{\infty}{\alpha^{-1}_{qp}} = e^{is\cdot\lambda x}\int u_p^*(x_1)\, e^{-isx_1}\, u_q(x_1)\, dx_1$$

$$= e^{i\lambda\bar{s}\cdot\bar{x}}\ \bar{\alpha}_{qp}(s)\ ;$$

$$(5.24)\quad \underset{\infty}{Q_{rs}}(x,x) = \underset{\infty}{\alpha^{-1}_{qp}}(x,x)\ e^{-i\lambda Ns\cdot x}$$

$$= e^{-i\lambda s\cdot x(N-1)}\ \bar{\alpha}_{qp}(s)\ .$$

But

$$(5.25)\quad Q_{rs}(x\ x) = e^{-is\cdot x\lambda(N-1)}\ \bar{Q}_{rs}(s)\ .$$

So our approximation of the inverse by the operator inverse in a complete basis, in the case of diagonal terms, gives the exact x dependence and only approximates the s dependence.

To apply our formalism to the harmonic oscillator in the case of two particles, the initial density matrix is

$$(5.26)\qquad \Gamma(x|y) = e^{-\alpha_0(x^2+y^2)}\ .$$

Using this in Eq. (5.14), we obtain

$$(5.27)\qquad e^{-\alpha_o(x^2+y^2)(L^2+\lambda^2)}\; e^{-\alpha_o(\frac{N^2\lambda^2}{2}-N\lambda^2)(x+y)^2}\;\cdot$$

$$\cdot\int dR\; e^{-\alpha_o[R^2\cdot 2(\lambda^2+c^2)+2\lambda R\cdot(x+y)(L+c[N-1])]}\;,$$

with $L = 1+\lambda$, $c = 1+(N-1)\lambda$. For $N = 2$, $c = L$.

Note that at $N = 2$, the $x\cdot y$ cross term which would make this expression a non legitimate density matrix vanishes.

For $N = 2$ carrying out the $R$ integration gives

$$(5.28)\qquad e^{-\alpha_o(x^2+y^2)(L^2+\lambda^2)}\left(\frac{\pi}{2\alpha_o(\lambda^2+L^2)}\right)^{3/2} e^{2\alpha_o\frac{\lambda^2L^2}{\lambda^2+L^2}(x+y)^2}\;,$$

which is a convergent quantity for all values of $\lambda$.

Let

$$(5.29)\qquad A = \alpha_o(L^2+\lambda^2)\quad\text{and}\quad B = \alpha_o\,4\lambda L\;.$$

For our case here

$$(5.30)\qquad \Gamma^{(2)} = \psi^*(x_1\;x_2)\cdot\psi(y_1\;y_2)$$

$$= e^{-A(x_1^2+x_2^2)-B\bar{x}_1\cdot\bar{x}_2}\cdot e^{-A(y_1^2+y_2^2)-B\bar{y}_1\cdot\bar{y}_2}\;,$$

by inspection of (5.28) when $N = 2$. This however is exactly the harmonic oscillator interacting wave function. This result which yields the exact form of the density matrix for the interacting harmonic oscillator case, to within the assignment of the parameters, is very unusual.

Aside from our approximation, in deriving our final formula, of the matrix element which should be good for large systems but poor for small systems the entire derivation assumed a determinantial form. For the $N = 2$ ground state due to separation of space and spin parts, the separate space part which is symmetric certainly does not satisfy this derivation. It therefore seems that the final equation has a wider validity than its derivation indicates. That this is so has been formally shown in the last part of Section 4.

We now wish to deal with atoms. The harmonic oscillator solutions, as they stand, have quadratic arguments and so do not give reasonable approximations to atomic states. However we may carry out the operation of letting the $r_i^2$ be transformed to linear arguments $\rho_i$. This transformation carries the noninteracting harmonic oscillator solution for two particles into the two particle noninteracting coulomb solution $\psi = e^{-b(\rho_1+\rho_2)}$. We note also that Schwinger has thus reduced the radial equation of the Kepler problem to the radial equation of the harmonic oscillator [10]. This leads us to expect that the same transformation applied in conjunction with our formalism will yield good correlation energy corrections for atomic systems. We carry this out by applying Eq. (5.14) to the harmonic oscillator case, and then carry out the $\bar{r}_i = \sqrt{\rho_i}\,\hat{\rho}_i$ transformation. Note that this is the case where our formalism gives exact results so our result is identical with that which would be obtained by operating directly on the interacting harmonic oscillator solution. The resulting trial wave function is therefore determined to be (by Eq. (5.30))

$$(5.31) \qquad \psi = N\, e^{-\frac{\alpha}{2}(\rho_1+\rho_2) - \frac{\beta}{2}\sqrt{\rho_1\rho_2}\,\hat{\rho}_1\cdot\hat{\rho}_2} \,.$$

Details of the calculation are presented in Appendix I. The value we obtain for the ground state energy is $E = -2.86765$ (for $\alpha_0 = 3.2520$ and $\lambda = 0.02014$), which is very close to the value obtained by the "harmonic atom" method in Section 6, and shows that our approach accounts for the correlation energy very well.

The direct application of our formalism to hydrogen-like orbitals for $N = 2$, using the ground state non-interacting one-body density matrix,

$$(5.32) \qquad \Gamma = e^{-\alpha_0(x+y)}$$

yields

$$(5.33) \; \langle x|\Gamma(1)|y\rangle = \int dR \;\exp\left\{-\alpha(\sqrt{x^2L^2+\lambda^2R^2+2x\cdot R\lambda L}\right.$$
$$\left. + \sqrt{R^2c^2+c\lambda R\cdot(-2x+N(x+y))+\lambda^2x^2+(\tfrac{N\lambda}{2})^2(x+y)^2-N\lambda^2x\cdot(x+y)}\right\}.$$

$$\cdot \exp\left\{- {}_{0}\left( \sqrt{y^2L^2+\lambda^2R^2+2y\cdot R\lambda L}\right.\right.$$

$$\left.\left. + \sqrt{R^2c^2+c\lambda R\cdot(-2y+N(x+y))+\lambda^2y^2+(\frac{N\lambda}{2})^2(x+y)^2-N\lambda^2y\cdot(x+y)}\right\};$$

set N = 2,

$$(5.34) \quad = \int dR \exp\left\{-\alpha_0\left( \sqrt{x^2L^2+\lambda^2R^2+2x\cdot R\lambda L}\right.\right.$$

$$\left.\left. = \sqrt{R^2L^2 + 2\lambda LR\cdot y + \lambda^2y^2}\right)\right\}$$

$$\cdot \exp\left\{-\alpha_0\left( \sqrt{y^2L^2+\lambda^2R^2+2y\cdot k\lambda L} + \sqrt{R^2L^2+2\lambda LR\cdot x+\lambda^2x^2}\right)\right\}$$

$$= \int dR \exp\left\{-2\alpha_0\left(\sqrt{x^2L^2+\lambda^2R^2+2\lambda Lx\cdot R} + \sqrt{y^2L^2+\lambda^2R^2+2\lambda L\bar{y}\cdot R}\right)\right\}.$$

We note in this case also that N = 2 has the special property — needed for a legitimate N = 2 density matrix, but not needed for N > 2, that the $\bar{x}\cdot\bar{y}$ terms cancel out.

Again, by inspection of (5.34) if we let $R \rightarrow x_2, y_2$ we can form a $\psi^*(x_1x_2)\ \psi(y_1y_2)$ which will yield this interacting density matrix. The wave function is

$$(5.35) \quad \psi(x_1x_2) = \exp\left\{- \alpha_0\left( \sqrt{x_1^2L^2+\lambda^2x_2^2+2\lambda L\bar{x}_1\cdot\bar{x}_2} + \right.\right.$$

$$\left.\left. + \sqrt{x_2^2L^2+\lambda^2x_1^2+2\lambda L\bar{x}_1\cdot\bar{x}_2}\right)\right\}$$

(neglecting normalization), which also satisfies the symmetry requirements.

This form of $\Gamma$, due to the angular argument under the square root sign, gives rise to difficult integrals, and we shall not use it for computations.

The transformation we have introduced gives an exact solution for the interacting harmonic oscillator case. It is reasonable to suppose that in the general case a sum of such solutions may give a reasonable wave function, i.e.

$$(5.36) \quad \psi^* = \sum_k g^*(\lambda_k) \operatorname{Det} u_p^*(y_i + \lambda_k \bar{y}') .$$

We may consider $\lambda$ a continuous parameter so that

$$(5.37) \qquad \psi(x_1 \ldots x_N) = \int g(\lambda) \operatorname{Det} u_p(x_i + \lambda \bar{x}') \, d\lambda \; .$$

This is recognized as a form of Eq. (3.7). Here we shall proceed by direct means to obtain the one and two particle density matrices in terms of the initial noninteracting density matrices.

Let us denote the N-th order density matrix of the system by

$$(5.38) \quad \langle \ldots x_i \ldots | \Gamma^{(N)}_{\bar{\lambda}} | \ldots y_i \rangle = \iint d\lambda \, d\lambda' \, g(\lambda) \, g^*(\lambda') .$$

$$\cdot \operatorname{Det} u_p(x_i + \lambda \bar{x}') \operatorname{Det} u_p^*(y_i + \lambda' \bar{y}')$$

$$= \int d\lambda \, d\lambda' \, g(\lambda) \, g^*(\lambda') \langle \ldots x_i \ldots | \Gamma^{(N)}_{\lambda\lambda'} | \ldots y_i \ldots \rangle$$

and the first order density matrix is (to within a normalization factor)

$$(5.39)\ \langle x|\Gamma^{(N)}_{\bar{\lambda}}(1)|y\rangle = \mathrm{Tr}_{2\ldots N}\langle\ldots x_i\ldots|\Gamma^{(N)}_{\lambda\lambda'}|\ldots y_i\ldots\rangle$$

$$= \int d\lambda\, d\lambda'\, g(\lambda)\, g^*(\lambda')\, \mathrm{Tr}_{2\ldots N}\langle\ldots x_i|\Gamma^{(N)}_{\lambda\lambda'}|\ldots y_i\ldots\rangle$$

$$= \int d\lambda\, d\lambda'\, g(\lambda)\, g^*(\lambda')\langle x|\Gamma^{(N)}_{\lambda\lambda'}(1)|y\rangle,$$

so that our previous formalism can be carried out and at the end we apply $\int d\lambda\, d\lambda'\, g(\lambda)\, g^*(\lambda')$ to the result. However we must make some slight modifications due to the presence of $\lambda$ and $\lambda'$.

$$(5.40)\ \langle x|\Gamma^{(N)}_{\bar{\lambda}}(1)|y\rangle = \iint d\lambda\, d\lambda'\, g(\lambda)\, g^*(\lambda')\cdot$$

$$\cdot \iint dR\, ds\, e^{-is\cdot R} \sum u_r(x+\lambda R+\lambda x)u_s^*(y+\lambda' R+\lambda' y)\cdot$$

$$\cdot\, Q'_{rs}[s,\lambda'(R+y),\lambda(R+x)]\ ,\quad \text{with } Q'_{rs} = \text{cofactor } (\alpha'_{rs}).$$

$$(5.41)\ \alpha'_{qp} = \int u_p^*(x_i+\lambda'[R+y])u_q(x_i+\lambda[R+x])\, dx_i\, e^{is\cdot x_i}$$

(due to $\lambda'$, $R$ remains in $Q'$);

$$= \langle u_p|e^{-\frac{i}{h}\lambda'(y+R)p}\, e^{is\cdot x_i}\, e^{\frac{i}{h}\lambda(x+R)p}|u_q\rangle .$$

So the operator

$$(5.42)\quad \alpha = e^{-\frac{is}{2}(\lambda'(y+R)+\lambda(x+R))} \cdot$$

$$\cdot\ e^{\{-\frac{i}{h}\lambda'(y+R)p+isx_i+\frac{i}{h}\lambda(x+R)p\}}.$$

For states of definite parity,

$$(5.43)\quad \text{Det}\ \alpha = e^{-i\frac{Ns}{2}(\lambda' y+\lambda x)-\frac{iNs}{2}R(\lambda+\lambda')},$$

$$(5.44)\quad \underset{\infty}{\alpha^{-1}_{qp}} = \int u_p^*(x_i+\lambda(R+x)\ e^{-is\cdot x_i}\ u_q(x_i+\lambda'(y+R))\ dx_i\ .$$

Now we use

$$(5.45)\quad Q'_{rs} \cong \underset{\infty}{\alpha^{-1}_{sr}}\ \det \alpha .$$

Let $\mathcal{A} = 1 + \frac{N}{2}(\lambda+\lambda')$, $\mathcal{B} = \frac{N}{2}(\lambda x+\lambda' y)$. Then

$$(5.46)\quad \langle x|\Gamma^{(N)}_{\bar{\lambda}}(1)|y\rangle = \iint d\lambda\ d\lambda'\ g(\lambda)\ g^*(\lambda')\cdot$$

$$\cdot \iint dR\ ds\ e^{-is\cdot(R\mathcal{A}+\mathcal{B})} \sum_{r,s}^{N,N} u_r(x[1+\lambda]+\lambda R)u_s^*(y[1+\lambda']+\lambda' R)\cdot$$

$$\cdot \int dx_1\ u_r^*(x_1+\lambda[R+x])\ e^{-is\cdot x_1}\ u_s(x_1+\lambda'[R+y])\ .$$

Take $\int ds \rightarrow \delta(\mathcal{A}R+\mathcal{B}+x_1)$. Then take $\int dx_1$ and get

$$(5.47)\quad \iint d\lambda\ d\lambda'\ g(\lambda)\ g(\lambda') \int dR \sum_{r,s} u_r(x[1+\lambda]+\lambda R)\cdot$$

$$\cdot\ u_r^*(-[\mathcal{A}R+\mathcal{B}]+\lambda[R+x])u_s(-[\mathcal{A}R+\mathcal{B}]+\lambda'[R+y])u_s^*(y[1+\lambda']+\lambda' R)=$$

$$= \iint d\lambda\, d\lambda'\, g(\lambda)\, g(\lambda') \int dR\, \Gamma(x+\lambda[x+R], -[\mathcal{A} R+\mathcal{B}]$$

$$+ \lambda[R+x])\, \Gamma(-[\mathcal{A} R+\mathcal{B}]+\lambda'[R+y], y+\lambda'[y+R]).$$

The expression for the two body density matrix can be obtained in exactly the same manner.

## 6. The Harmonic Atom.

Since the intrinsic state approach can be used without approximation for harmonic internal and external potentials by working with orbital annihilators and creators, the same would hold for any set of orbitals. This is identical to choosing as an ansatz a one body unitary transform of a totally harmonic atom. Such an ansatz clearly has an invariant characterization consisting of the eigenvalues of the one body density matrix and the full two body density matrix in the $\Gamma_1$ representation. To see if these are reasonable for application to atoms let us first look at the two body problem. For a two-electron system, with opposite spin, the space wave function is symmetric and we may define the symmetric matrix

$$(6.1)\qquad \langle 1|\psi|2\rangle \equiv \psi(1,2)\ .$$

Hence the one body density matrix is given by

$$(6.2)\qquad \Gamma_1 = 2\psi\psi^* .$$

If also $\psi$ is real then the real orthogonal transformation which diagonalizes $\psi$ diagonalizes $\Gamma_1$, and this is our case. Now

$$(6.3)\ \langle 1|\psi|2\rangle = \left(\frac{A^2-B^2}{\pi^2}\right)^{3/4} e^{-\frac{A}{2}(r_1^2+r_2^2)+B\bar{r}_1\cdot\bar{r}_2}$$

for the interacting ground state. J. K. Percus has shown that the eigenvalues of the density matrix go as $c_0 e^{(n_1+n_2+n_3)c}$ and I have checked that the results obtained are quite close to those for the helium calculation by Auffray and Sobol[8]. $\Gamma_2 = \psi(1,2)\ \psi^*(1'2')$ in the same representation does not have the correct sign for all elements, but of course does for the crucial diagonal ones. The method thus should give reasonable results. A possible approach to the N body problem with interaction thus is available to us. The noninteracting density matrix for N particles in a harmonic well as given by Eq. (4.20) can by the formalism in Eq. (4.27) be transformed to the interacting harmonic oscillator density matrix. We would then desire to use unitary transformations to a more appropriate set of orbitals. We shall now study this problem in a more direct manner, and its application.

Consider a system for which the solution $\phi(1\ldots N)$ is associated with the solution for another physical system $\psi(1'\ldots N')$ by means of the unitary transformation $U(1\ldots N,1'\ldots N')$.

$$(6.4)\quad \phi(1\ldots N) = \int U(1\ldots N,1'\ldots N')\psi(1'\ldots N')\, dx_N.$$

The density matrix for $\phi$ will then be given by

$$(6.5)\quad \Gamma_\phi(1'2'|1\,2) = \iiint \psi^*(1''\ldots N'')U^*(1''\ldots N''|1',2',3'''\ldots)$$

$$U(1,2,3'''\ldots N'''|1^{iv},2^{iv}\ldots N^{iv})\psi(1^{iv}\ldots N^{iv})(dx'')(dx^{iv})(dx_{12}''') .$$

This would represent an exact solution. On the other hand, reducing our U's to product U's, and our $\psi$'s to antisymmetrized products, we would obtain a solution of the Slater determinant type in which electronic correlation is neglected. We will introduce correlation by retaining the model wave function in its interacting form but assuming that a reasonable approximation to the true solution can be obtained using U's of single particle forms i.e.

$$(6.6)\qquad U(1\ldots N|1'\ldots N') = \prod_{i,i'=1}^{N} U(i,i') .$$

With this assumption,

$$(6.7)\quad \int U^*(1^0\ldots N^0|1^1,2^1,3'\ldots N')U(1'\ldots N'|1\,2\,3\ldots N)(dx_{1'2'})$$

$$= U^*(1^0 1^1)U^*(2^0 2^1)U(1'1)U(2'2) \prod_{i\neq 1,2} \delta(i^0-i) .$$

So

$$(6.8)\quad \Gamma_\phi(1'2'|1\,2) = \int U^*(1^0 1')U^*(2^0 2')$$

$$\cdot\ \Gamma_\psi(1^0 2^0|1''2'')U(1\,1'')U(2\,2'')\ d1^0\ d2^0\ d1''\ d2''$$

and

$$(6.9)\qquad E_\phi = \int \Gamma_\psi(1^0 2^0|1''2'')[\int U^*(1^0 1')U^*(2^0 2')$$

$$\cdot H(1\,2)U(1\,1'')U(2\,2'')\ d1\ d2]\ d1^0\ d2^0\ d1''\ d2'' ,$$

where

$$(6.10) \qquad H(1\ 2) = N\ H(1) + \frac{N(N-1)}{2}\ V(1\ 2)\ .$$

H(1) are the one body terms of the Hamiltonian and V(1 2) are the interaction terms.

The simplest application of our formalism is to let our unitary transformation be

$$(6.11) \qquad U(1,1') = \delta(1-1')\ .$$

Applying this to the wave function of the central harmonic oscillator potential with harmonic oscillator interactions between the two particles will yield a poor estimate of the energy but will give a clear indication of the dependence of the energy on the interparticle interaction of our model.

The wave function used is

$$(6.12) \qquad \psi = N\psi_U = N\ e^{-\frac{A}{2}(r_1^2+r_2^2)+B\bar{r}_1\cdot\bar{r}_2} \quad \text{where } N^2 = \left(\frac{A^2-B^2}{\pi^2}\right)^{3/2}$$

as

$$(6.13)\ N^2 \int \psi_U^* \psi_U\ d1\ d2 = N^2(4\pi)^2 \int_0^\infty \int_0^\infty e^{-A(r_1^2+r_2^2)}\ .$$

$$\cdot\ \frac{\sinh 2Br_1r_2}{2B}\ r_1r_2\ dr_1\ dr_2$$

$$= N^2\ 4\pi\left(\frac{\pi}{A}\right)^{3/2} \int_0^\infty r_1^2\ e^{-(A-B^2/A)r_1^2}\ dr_1 \ = \ 1\ .$$

$$(6.14) \quad E = \int \psi^*(1\ 2)H(1\ 2)\psi(1\ 2)\ d1\ d2$$

$$H(1\ 2) = -\frac{h^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{1\ 2}}$$

Considering the kinetic energy, potential energy and interaction energy separately we obtain

$$(6.15) \quad \frac{h^2}{2m}\int \psi^*(-\nabla_1^2-\nabla_2^2)\psi\ d1\ d2 = \frac{h^2}{m}\cdot\frac{3A}{2} \quad .$$

$$\int \psi^*\left(-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}\right)\psi\ d1\ d2 = -4Ze^2\sqrt{\frac{A^2-B^2}{\pi A}}$$

$$\int \psi^*\left(\frac{e^2}{r_{12}}\right)\psi\ d1\ d2 = e^2\sqrt{\frac{2(A+B)}{\pi}}$$

So in a.u.

$$(6.16) \qquad E = \frac{3A}{2} - 8\sqrt{\frac{A^2-B^2}{\pi\ A}} + \sqrt{\frac{2(A+B)}{\pi}} \quad .$$

In terms of the strength of the central potential k and the interacting potential K,

$$(6.17) \qquad E = \frac{3}{4}\left[\sqrt{k+2K} + \sqrt{k}\ \right] - 4Z\sqrt{\frac{2\sqrt{k+2K}\cdot\sqrt{k}}{\pi(\sqrt{k+2K}+\sqrt{k}\ )}} + \sqrt{\frac{2\sqrt{k+2K}}{\pi}} \quad .$$

For K = 0, setting $\partial E/\partial k = 0$, we find the minimum for

(6.18) $\sqrt{\alpha} = \frac{2}{3} \left( \frac{1}{\sqrt{2\pi}} - \frac{2Z}{\sqrt{\pi}} \right)$ where $\alpha = \sqrt{k}$ ,

so $E \cong -2.3002$ a.u. for $k \sim 2.353$.

If K is positive and increases the energy gets larger.

If K is negative and $|K|$ increases the energy decreases.

The minimum of -2.32389 a.u. occurs at $k = 2.8680$, and $K = -0.4460$.

A plot of the variation of the energy versus K with k fixed yields a parabolic form and the same is true for the energy versus B with A fixed.

We see that we get an improvement in the energy of -0.023 a.u. The main point is that the variation in energy follows the model in the sense that when K is positive, representing an attractive interaction between the particles which does not correspond to the helium atom, the correlation introduced increases the energy. However when K becomes negative the energy is lowered by the correlation introduced as it corresponds more closely to the correct correlation effect for Helium. The overall energy value we have obtained is very poor due to our using the harmonic oscillator wave function directly. We therefore must use a more reasonable unitary transformation U(1,1').

When the simple product model

(6.19) $\psi_{H.F.} = N e^{-b(r_1+r_2)} = v_0(1)v_0(2)$ , which is a solution for the helium atom without electronic interaction is used to obtain the energy, the minimum value obtained is $E = -2.8476560$ a.u. for $b = 27/16 = 1.68750$, which is a very good result as the true energy is $-2.9037$ a.u. We therefore seek a $U(1,1')$ such that the correlated wave function it produces will reduce to $\psi_{H.F.}$ as the electronic interaction goes to zero in our model i.e. $\psi_{H.O.} \to u_0(1)u_0(2)$ a product form.

Ideally we would use

$$(6.20) \qquad U(1'1) = \sum_{i=0}^{\infty} v_i(1')u_i^*(1) .$$

As this form is not known to us we will use a U which will meet our specifications with respect to the ground state but will connect modified sets for higher states. Such a U is

$$(6.21) \quad U(1,1') = (1-1') - \frac{u_0(1)-v_0(1)}{1-\int u_0(2)v_0^*(2)d2} [u_0^*(1')-v_0^*(1')] .$$

A detailed calculation using this $U(1\ 1')$ follows in the application of the formalism to the calculation of the ground state energy of helium.

The integral expressions for the energy, E, can be set up in two equivalent forms in our formalism.

$$(6.22)\quad E = \int \psi^*(1''2'')[\int U^*(1''1)U^*(2''2)\ H(1\ 2)U(1\ 1')U(2\ 2')d1d2]$$

$$\cdot\ \psi(1'2')\ d1'\ d2''\ d2'\ d1''$$

$$= \frac{2}{N(N-1)} \int \Gamma_\psi(1''2''|1'2')[\int U^*(1''1)U^*(2''2)H(1\ 2)\cdot$$

$$\cdot\ U(1\ 1')\ U(2\ 2')\ d1\ d2]\ d1'\ d2'\ d1''\ d2''\ .$$

$$(6.23)\quad E = \int \phi^*(1\ 2)\ H(1\ 2)\ \phi(1\ 2)\ d1\ d2$$

with

$$\phi(1\ 2) = \int U(1\ 1')\ U(2\ 2')\ \psi(1'\ 2')\ d1'\ d2'.$$

The single particle product wave function to be used as our approximation for the helium wave function in constructing our single particle unitary operators $U(1\ 1')$ is

$$(6.24)\qquad \psi_{H.F.} = v_0(1)\ v_0(2) = \frac{b^3}{\pi}\ e^{-b(r_1+r_2)}\ .$$

The noninteracting harmonic oscillator wave function for two particles

$$(6.25)\qquad \psi_{H.O.} = u_0(1)\ u_0(2) = (\frac{\alpha}{\pi})^{3/2}\ e^{-\frac{\alpha}{2}(r_1^2+r_2^2)}$$

is also used to construct U in such a manner that if $\psi_{H.O.}$ is substituted for $\psi$ in (6.22) $\phi$ in (6.23) becomes $\psi_{H.F.}$.

To improve our energy estimate we will operate on an "interacting" wave function to take care of the effect of correlation between the electrons. We can denote the unitary form (6.21) by

$$(6.26)\quad U(1\,1') \equiv \delta(1-1') - A(1\,1')$$

$$\equiv \delta(1-1') - \mathcal{A}(1) * \mathcal{A}^*(1') \;.$$

Note in our case the quantities are real, so $u_0^* = u_0$, $v_0^* = v_0$.

$$(6.27)\qquad \mathcal{A}(1) = \frac{u_0(1)-v_0(1)}{\sqrt{1 - \int u_0\, v_0\, d2}} \quad ,$$

where

$$(6.28)\quad \int u_0(1)v_0(1)\; d1 = \left(\frac{\alpha}{\pi}\right)^{3/4}\left(\frac{b^3}{\pi}\right)^{1/2} * 4\pi \int_0^\infty e^{-\frac{\alpha}{2}r_1^2-br_1}\; r_1^2 dr_1$$

$$= 4\,\frac{\alpha^{3/4}b^{3/2}}{\pi^{1/4}}\left[-\frac{b}{\alpha^2} + \sqrt{\frac{\pi}{2\alpha}}\; e^{-b^2/2\alpha}\left(\frac{1}{\alpha} + \frac{b^2}{\alpha^2}\right)\mathrm{erfc}\left(\frac{b}{\sqrt{2\alpha}}\right)\right] \;.$$

The interacting wave function to be used is a solution of the interacting harmonic oscillator problem with the Hamiltonian

$$(6.29)\qquad H_K = \sum_i \left(\frac{p_i^2}{2m} + \frac{k}{2}\,x_i^2\right) + \frac{K}{2}\sum (x_i-x_j)^2 \;,$$

where we shall also have K take on negative values.

The symmetric ground state solution is

$$(6.30) \qquad \psi_K = N\, e^{-\frac{\beta}{\alpha}\sum^N x_i^2 + \frac{1}{2N}(\beta-\alpha)(\sum^N x_i)^2} ,$$

with $\alpha = m\omega/\hbar = \sqrt{mk}/\hbar \quad (k = m\omega^2)$, $\beta = \sqrt{m(k+NK)}/\hbar$ .
For N = 2,

$$(6.31) \qquad \psi_K = \left(\frac{A^2-B^2}{\pi^2}\right)^{3/4} e^{-\frac{1}{2}A(r_1^2+r_2^2)+B(\bar{r}_1\cdot\bar{r}_2)} ,$$

with $A = \frac{1}{2}(\alpha+\beta)$, $B = \frac{1}{2}(\beta-\alpha)$.

The wave function, $\psi_K$, is now used with H(1 2) for helium in Eq. (6.23). The details of the calculation are given in Appendix II. Part of the integration involved was carried out numerically on the computer. Varying the parameters led to a minimum energy of -2.868 a.u. for k = 1.4 and K = -0.13, representing an improvement of 0.02 a.u. over the uncorrelated wave function with K = 0. This improvement is close to fifty percent of the total correlation energy of 0.042 a.u. [5]. If we apply a unitary transformation to get us to the best Hartree state then our uncorrelated starting base will be - 2.86167 a.u. [7] so our energy value will be around -2.88167 with the use of only two variable parameters. This is probably the best value that can be obtained on the basis of a unitary transformation approach, and only two parameters. It can be seen immediately by using a natural spin orbital expansion for the first order density matrix i.e.

$$\Gamma(x_1', x_1) = \sum \eta_k \; {}^{*}_{k}(x_1') \; {}_{k}(x_1)$$

that the $\eta_k$, which are the eigenvalues of the $\Gamma$ matrix used as an operator with integration, cannot be altered by a one body unitary transformation. This in part explains our inability to obtain the total correlation energy. As noted previously a comparison of the magnitudes of the harmonic oscillator density matrix eigenvalues with those of helium, as obtained by Sobol [8], showed the magnitudes of the eigenvalues in both cases to be fairly close.

The unitary transformation used in this calculation was constructed to transform the noninteracting harmonic oscillator ground state into the noninteracting helium ground state. However it did not carry out the same correspondence to higher states. That this fact did not affect the results much will be seen by a comparison with the results of our completely independent calculation on helium using the oscillator based density matrix, with only two parameters, which yields the same minimum value of $E = -2.868$ a.u.

Given a good closed form of U, calculations for large atoms can be carried out in the same manner. The U used in the present helium calculation is not suitable for larger systems. However, the feasability and effectiveness of this approach have been demonstrated.

## Summary

We have presented approaches for improving the calculation of energy values for atoms by accounting for the inter-particle correlation. The projection of symmetry breaking intrinsic states was studied in this connection. The more powerful approach of intrinsic state density matrices was then developed. Oscillator based density matrices were then studied and a useful approximation technique was developed for their application. The formalism was applied with the use of an additional transformation to the case of helium to show the improvement resulting from it.

A direct harmonic atom approach was then studied. Unitary transformations allowed one to obtain a large class of one-body density matrices, and guaranteed realizable two-body density matrices. This formalism was also tested on helium and shown to give results similar to those obtained by our previous technique.

# Appendix I. Details of the Application to Helium of the Ansatz Wave Function Arising from Our Transformation of the Oscillator-Based Density Matrix.

We here present details of the application to helium of the ansatz wave function arising from our transformation of the oscillator-based density matrix. Our trial wave function is given by

$$(\mathrm{I}.1)\qquad \psi = Ne^{-\frac{\alpha}{2}(r_1+r_2)-\frac{\beta}{2}(\sqrt{r_1r_2})r_1\cdot r_2} ,$$

with the Hamiltonian

$$(\mathrm{I}.2)\qquad H = -\frac{h^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{1\,2}} .$$

In the $\beta = 0$ case, we have the simple

$$(\mathrm{I}.3)\qquad \psi_0 = \frac{1}{\pi}\left(\frac{\alpha_0}{2}\right)^3 e^{-\frac{\alpha_0}{2}(r_1+r_2)} ,$$

which yields a minimum energy of E = -2.8476565 a.u. for $\alpha_0 = 3.37500$. We note at this point that the best value obtained for the solution of the non-relativistic Schrodinger equation is E = -2.9037 a.u.

In carrying out our calculations the transformations that it is convenient for us to use are as follows:

$$\text{(I.4)} \qquad \bar{r} = \rho\,\bar{\rho} \;,\quad x_i = \rho\rho_i \;,\quad \rho_i = \frac{x_i}{\sqrt{r}} \;,\quad r = \rho^2 ,$$

$$\sqrt{r} = \rho \;,\quad \sqrt{r}\,\hat{r} = \bar{\rho} \;;$$

$$\text{(I.5)} \qquad \frac{\partial\rho_i}{\partial x_j} = \frac{\delta_{ij}}{\delta} - \frac{\rho_i\rho_j}{2\rho^3} \;,\qquad \frac{\partial x_j}{\partial\rho_i} = \frac{\rho_i\rho_j}{\rho} + \delta_{ij}\,\rho \;.$$

These relations can be checked using

$$\text{(I.6)} \qquad \sum_i \frac{\partial x_j}{\partial\rho_i}\frac{\partial\rho_i}{\partial x_j} = 1 \;.$$

The Jacobian for transforming from the x -> $\rho$ system,

$$\text{(I.7)} \qquad J = \frac{\partial(x\ y\ z)}{\partial(\rho_x\rho_y\rho_z)} = 2\,\rho^3 \;.$$

$$\text{(I.8)} \qquad \frac{\partial}{\partial x_k} = \sum_i \frac{\partial\rho_i}{\partial x_k}\,\frac{\partial}{\partial\rho_i} \;.$$

So

$$\text{(I.9)} \qquad \iint \bar{\nabla}_1\,\psi^*(r_1r_2)\cdot\nabla_1\psi(r_1r_2)\;d^3r_1\;d^3r_2$$

$$= \iint \sum_k \sum_{i,j} \frac{\partial\rho_i}{\partial x_k}\frac{\partial\rho_j}{\partial x_k}\,\frac{\partial}{\partial\rho_j}\,\psi^*(\rho_a^2\rho_b^2)\,\frac{\partial}{\partial\rho_i}\,\psi(\rho_a^2\rho_b^2)\;\cdot$$

$$\cdot\; J_aJ_b\;d^3\rho_a\;d^3\rho_b\;; \qquad\qquad \rho_i \equiv \rho_{ai}\;.$$

$$\text{(I.10)} \qquad \sum_k \frac{\partial\rho_i}{\partial x_k}\frac{\partial\rho_j}{\partial x_k} = \frac{\delta_{ij}}{\rho^2} - \frac{3\rho_i\rho_j}{4\rho^4}\;.$$

$$(\text{I.11}) \qquad \frac{\partial}{\partial\rho_{ai}} \; e^{-\frac{\alpha}{2}(\rho_a^2+\rho_b^2)-\frac{\beta}{2}\bar{\rho}_a\cdot\bar{\rho}_b} =$$

$$= \frac{\psi(\rho_a^2\rho_b^2)}{N}\left[-\alpha\,\rho_{ai} - \frac{\beta}{2}\,\rho_{bi}\right] ,$$

for our original $\psi(r_1r_2) = N\,e^{-\frac{\alpha}{2}(r_1+r_2)-\frac{\beta}{2}(\sqrt{r_1r_2})\hat{r}_1\cdot\hat{r}_2}$ for helium.

Our total expression for Equation (I.9) now is

$$(\text{I.12}) \qquad N^2 \iint e^{-\alpha(\rho_a^2+\rho_b^2)-\beta\bar{\rho}_a\cdot\bar{\rho}_b} \,\cdot$$

$$\cdot\left[\alpha^2+\beta^2\left(\frac{\rho_b^2}{\rho_a^2} - \frac{3}{4}\,\frac{(\bar{\rho}_a\cdot\bar{\rho}_b)^2}{\rho_a^4}\right) + \alpha\beta\,\frac{\bar{\rho}_a\cdot\bar{\rho}_b}{\rho_a^2}\right] \rho_a^3\rho_b^3\, d^3\rho_a d^3\rho_b .$$

(The parts in brackets will be considered separately and designated as 1a, 1d, 1b, 1c respectively.)

Now consider the integrals needed to evaluate the energy. Let

$$(\text{I.13}) \qquad K_{\alpha\beta} = e^{-\alpha(\rho_a^2+\rho_b^2)-\beta\bar{\rho}_a\cdot\bar{\rho}_b} ,$$

and

$$(\text{I.14}) \qquad I_N(\alpha,\alpha,\beta) = \iint e^{-\alpha(\rho_a^2+\rho_b^2)}\,\rho_a^4\,\rho_b^4 \sinh(\beta\,\rho_a\rho_b)\,d\rho_\alpha d\rho_\beta ,$$

so our normalization condition is

$$(\text{I.15}) \qquad 1 = N^2 \int K_{\alpha\beta}\; 4\;\rho_a^5\;\rho_b^5\; d\rho_a\; d\rho_b\; d\Omega_a\; d\Omega_b$$

$$= N^2\cdot 4\cdot \frac{(4\pi)^2}{\beta}\; I_N(\alpha,\alpha,\beta) .$$

In atomic units ($e = h = m = 1$, $a_0 = 1$) the energy

$$(I.16) \qquad E = \int \nabla_1 \psi^* \bar{\nabla}_1 \psi \, dl \, ds - 2 Z \int \psi^* \frac{1}{r_1} \psi \, dl \, ds + \\ + \int \psi^* \frac{1}{r_{1\,2}} \psi \, dl \, ds ,$$

the parts of which we designate as 1, 2, 3.

Part 3 we consider separately; parts 1 and 2 can be written out as follows, with $dV_{ab} = d\rho_a \, d\rho_b \, d\Omega_a \, d\Omega_b$,

$$1a \quad = \alpha^2/4 ;$$

$$1b \quad = - \frac{3}{4} \beta^2 N^2 \iint K_{\alpha\beta} (\bar{\rho}_a \cdot \bar{\rho}_b)^2 \rho_a \rho_b^5 \, dV_{ab} ;$$

$$1c \quad = \alpha\beta N^2 \iint K_{\alpha\beta} (\bar{\rho}_a \cdot \bar{\rho}_b) \rho_a^3 \rho_b^5 \, dV_{ab} ;$$

$$1d \quad = \beta^2 N^2 \iint K_{\alpha\beta} \rho_a^3 \rho_b^7 \, dV_{ab} ;$$

$$2 \quad = 2Z \cdot 8N^2 \iint K_{\alpha\beta} \rho_a^3 \rho_b^5 \, dV_{ab} .$$

The angular integrations are carried out using the following equations:

$$(I.17) \qquad \int_{s_1} \int_{s_2} e^{-B(\bar{e}_1 \cdot \bar{e}_2)} \, d\Omega_{e_1} \, d\Omega_{e_2} = (4\pi)^2 \frac{\sinh B}{B} ;$$

$$(I.18) \qquad \int_{s_1} \int_{s_2} e^{-B(\bar{e}_1 \cdot \bar{e}_2)} \, \bar{e}_1 \cdot \bar{e}_2 \, d\Omega_{e_1} \, d\Omega_{e_2} = (\frac{4\pi}{B})^2 \sinh B - \\ - \frac{(4\pi)^2}{B} \cosh B ;$$

$$(\mathrm{I}.19)\quad \int_{S_1}\int_{S_2} e^{-B(\bar{e}_1\cdot\bar{e}_2)}(\bar{e}_1\cdot\bar{e}_2)^2\, d\Omega_{e_1}\, d\Omega_{e_2} = \frac{(4\pi)^2}{B}\left\{(\frac{2}{B^2}+1)\sinh B - \frac{2}{B}\cosh B\right\} .$$

The resulting integrals can then be completed by using the results of Table I.

We now consider the integration integral (3):

$$N^2 \iint e^{-\alpha(r_1+r_2)-\beta\sqrt{r_1r_2}\, r_1\cdot r_2}\, \frac{e^2}{r_{12}}\, d^3r_1\, d^3r_2 .$$

The angular integrals will depend on the sign of $\beta$. We have

$$(\mathrm{I}.20)\quad \begin{Bmatrix}\mathcal{A}_D\\ \mathcal{A}_\phi\end{Bmatrix} = \iint \frac{e^{\mp|\beta|\sqrt{r_1r_2}\,\hat{r}_1\cdot\hat{r}_2}\, d\Omega_1\, d\Omega_2}{r_{12}}$$

$$= \frac{8\pi^2}{(r_1r_2)^{3/4}}\, e^{\mp\beta(r_1^2+r_2^2)/2\sqrt{r_1r_2}}\sqrt{\frac{2}{|\beta|}}\int_c^d e^{\pm x^2}\, dx,$$

where $c = \sqrt{\dfrac{|\beta|}{2\sqrt{r_1r_2}}}\cdot|r_1-r_2|$ and $d = \sqrt{\dfrac{|\beta|}{2\sqrt{r_1r_2}}}\cdot|r_1+r_2|$.

Let

$$(\mathrm{I}.21)\quad D(\alpha) = \int_0^\alpha e^{x^2}\, dx\ ;\quad \phi(\alpha) = \int_0^\alpha e^{-x^2}\, dx\ ;$$

$$\mathcal{E}(\alpha) = \begin{Bmatrix} D(\alpha)\\ \phi(\alpha)\end{Bmatrix} .$$

Use $N^2 = \beta/4(4\pi)^2 I_N$ (for $\beta \neq 0$) with the scalar transformation $r = \rho^2$, $dr = 2\rho \; d\rho$ .

$$\begin{matrix}3a)\\ b)\end{matrix} \quad = \frac{e^2}{2I_N}\sqrt{2\beta}\iint e^{-\alpha(\rho_a^2+\rho_b^2)}\rho_a^3\rho_b^3\sqrt{\rho_a\rho_b}$$

$$\cdot \; e^{\mp|\beta|(\rho_a^4+\rho_b^4)/2\rho_a\rho_b} \, d\rho_a \; d\rho_b \; .$$

$$\cdot \; [\mathcal{E}\,(\overbrace{\sqrt{\frac{|\beta|}{2\rho_a\rho_b}}\;|\rho_a^2+\rho_b^2|)}^{BP} - \mathcal{E}\,(\overbrace{\sqrt{\frac{|\beta|}{2\rho_a\rho_b}}\;|\rho_a^2-\rho_b^2|)}^{BN}\;] \; .$$

For (3a), use the definitions

$$\mathcal{D}(\alpha) = e^{-\alpha^2}\int_0^\alpha e^{t^2}\,dt = \mathrm{DAWF}(\alpha); \quad \mathrm{ERF}(\alpha) = e^{\alpha^2}\int_0^\alpha e^{-t^2}\,dt$$

$$3a) = \frac{e^2}{I_N}\sqrt{\frac{\beta}{2}}\iint \rho_a^3\rho_b^3\sqrt{\rho_a\rho_b}\,[e^{-\alpha(\rho_a^2+\rho_b^2)+\beta\rho_a\rho_b}\mathcal{D}(BP)$$

$$- \; e^{-\alpha(\rho_a^2+\rho_b^2)-\beta\rho_a\rho_b}\mathcal{D}(BN)] \, d\rho_a \; d\rho_b \quad ,$$

and

$$3b) = \frac{e^2}{I_N}\sqrt{\frac{\beta}{2}}\iint \rho_a^3\rho_b^3 \; \sqrt{\rho_a\rho_b}\;[e^{-\alpha(\rho_a^2+\rho_b^2)-\beta\rho_a\rho_b}\;\mathrm{ERF}(BP)$$

$$- \; e^{-\alpha(\rho_a^2+\rho_b^2)+\beta\rho_a\rho_b}\;\mathrm{ERF}(BN)] \, d\rho_a \; d\rho_b \; .$$

These expressions were evaluated numerically.

Let $K_{abc} = e^{-\frac{1}{2}(a^2x^2+b^2y^2-cabxy)}$,

with $a > 0,\ b > 0,\ |c| < 1.$

$$\mathcal{I}_v \equiv \int_0^\infty\int_0^\infty (x\ y)^v\ K_{abc}\ dx\ dy.$$

## Table I

$$\mathcal{I}_0 = \frac{1}{ab\sqrt{1-c^2}} \cos^{-1} c$$

$$\mathcal{I}_1 = \frac{1}{(ab)^2} \left[ \frac{1}{1-c^2} - \frac{c \cos^{-1} c}{(1-c^2)^{3/2}} \right]$$

$$\mathcal{I}_2 = \frac{1}{(ab)^3} \left[ -\frac{3c}{(1-c^2)^2} + \frac{\cos^{-1} c}{(1-c^2)^{3/2}} + \frac{3c^2 \cos^{-1} c}{(1-c^2)^{5/2}} \right]$$

$$\mathcal{I}_3 = \frac{1}{(ab)^4} \left[ \frac{4}{(1-c^2)^2} + \frac{15c^2}{(1-c^2)^3} - \frac{9c \cos^{-1} c}{(1-c^2)^{5/2}} - \frac{3\cdot 5c^3 \cos^{-1} c}{(1-c^2)^{7/2}} \right]$$

$$\mathcal{I}_4 = \frac{1}{(ab)^5} \left[ -\frac{55c}{(1-c^2)^3} - \frac{7\cdot 15\ c^3}{(1-c^2)^4} + \frac{9 \cos^{-1} c}{(1-c^2)^{5/2}} + \right.$$

$$\left. + \frac{2\cdot 5\cdot 9\ c^2 \cos^{-1} c}{(1-c^2)^{7/2}} + \frac{3\cdot 5\cdot 7\ c^4 \cos^{-1} c}{(1-c^2)^{9/2}} \right]$$

## Appendix II. Details of the Application to Helium of the Harmonic Atom Approach.

We here present details of the application to helium of the harmonic atom approach. The expressions in Eq. (6.22) are expanded by the use of (6.26). Using considerations of symmetry in the hamiltonian the following breakup is obtained:

$$\int \psi^*(1''2'')\ [\int U\ U\ H\ U\ U\ d1\ d2]\ \psi(1'2')\ d1'd2'd1''d2''$$

$$= \int \psi^*(1''2'')\ H(1''2'')\ \psi(1''2'')\ d1''\ d2'' \qquad \text{I}$$

$$- 2\int \psi^*(1\ 2')\ H(1)\ A(1\ 1')\ \psi(1'2')\ d1\ d1'\ d2' \qquad \text{IIa}$$

$$- 2\int \psi^*(1''2')\ A(1''1)H(1)\psi(1\ 2')\ d1\ d1''\ d2' \qquad \text{IIb}$$

$$+ 2\int \psi^*(1''2')\ A(1''1')\ \bar{H}(1)\ \psi(1'2')\ d1''\ d1'\ d2' \qquad \text{IIc}$$

$$- 4e^2\int \psi^*(1\ 2)\ A(2\ 2')\ \frac{1}{r_{12}}\ \psi(1\ 2')\ d1\ d2\ d2' \qquad \text{III}$$

$$+ 2e^2\int \psi^*(1\ 2'')\ A(2''2)\ A(2\ 2')\ \frac{1}{r_{12}}\ \psi(1\ 2')\ d1\ d2\ d2'\ d2'' \qquad \text{IV}$$

$$+ 2e^2\int \psi^*(1\ 2)\ A(1\ 1')\ A(2\ 2')\ \frac{1}{r_{12}}\ \psi(1'2')\ d1\ d1'\ d2\ d2' \qquad \text{V L1}$$

$$+ 2e^2\int \psi^*(1\ 2'')\ A(1\ 1')\ A(2''2)\ \frac{1}{r_{12}}\ \psi(1'2)\ d1\ d1'\ d2\ d2'' \qquad \text{V L2}$$

$$- 4e^2 \int \psi^*(1\ 2'')\ A(1'1)\ A(2''2)\ A(2\ 2')\ \frac{1}{r_{12}}\ \psi(1'2')\ d1\ d1'\ d2\ d2'\ d2'' \qquad \text{V L3}$$

$$+ e^2 \int \psi^*(1''2'')\ A(1''1)\ A(1\ 1')\ \frac{1}{r_{12}}\ A(2''2)\ A(2\ 2')\ \psi(1'2')\ d1\ d1'\ d1''\ d2\ d2'\ d2'' \qquad \text{V L4}$$

where

$$\text{(II.1)} \qquad \psi = \left( \frac{A^2-B^2}{\pi^2} \right)^{3/4} e^{-\frac{A}{2}(r_1^2+r_2^2)+B\bar{r}_1\cdot\bar{r}_2} \ ;$$

$$\text{(II.2)} \qquad H(1\ 2) = H(1) + H(2) + \frac{e^2}{r_{1\ 2}} \ ;$$

$$\text{(II.3)} \qquad \bar{H}(1) = - \frac{h^2}{2m}\ \bar{c}(\nabla_1^2) - z\ e^2\ \bar{c}\left(\frac{1}{r_1}\right) \ ;$$

$$\text{(II.4)} \qquad \bar{\mathcal{O}} = \int \mathcal{A}(1)\ \mathcal{O}\ \mathcal{A}(1)\ d1 \ ;$$

$$\text{(II.5)} \qquad A(1\ 2) = \mathcal{A}(1)\ \mathcal{A}(2) \ .$$

Some parts of these integrals are not integrable analytically. So the integrals will be reduced to double integrals for which I have developed integration routines for the computer on the basis of a double Simpsons rule. A part of this reduction is most easily evident by examining (6.23).

Let

$$(\mathrm{II}.6) \qquad \mathcal{B}(1) = \int \mathcal{A}(2)\ \psi(1\ 2)\ d2$$

$$(\mathrm{II}.7) \qquad \begin{aligned} \phi(1\ 2) &= \int U(1\ 1')\ U(2\ 2')\ \psi(1'2')\ d1'\ d2' \\ &= \psi(1\ 2) - \mathcal{A}(2)\mathcal{B}(1) - \mathcal{A}(1)\mathcal{B}(2) \\ &\quad + A(1\ 2) \underbrace{\int \mathcal{A}(2')\mathcal{B}(2')\ d2'}_{\mathrm{TAB}} . \end{aligned}$$

Now take $\phi(1\ 2) \cdot \phi(1\ 2)$. When this expression is integrated or is multiplied by a symmetric term like $1/r_{12}$ and then integrated we can by symmetry reduce the integrals to sevel terms. These seven terms can be identified with all the $1/r_{12}$ terms of our previous breakup and could be obtained by further integration.

$$\begin{aligned} (\mathrm{II}.8) \quad & \underbrace{\psi(1\ 2)\ \psi(1\ 2)}_{[\text{Part of I}]} - \underbrace{4\psi(1\ 2)\mathcal{A}(1)\mathcal{B}(2)}_{[\mathrm{III}]} + \underbrace{2\psi(1\ 2)A(1\ 2)\mathrm{TAB}}_{[\mathrm{V\ L1}]} \\ & + \underbrace{2[\mathcal{A}(2)\mathcal{B}(1)]^2}_{[\mathrm{IV}]} + \underbrace{2\mathcal{A}(2)\mathcal{B}(1)\mathcal{A}(1)\mathcal{B}(2)}_{[\mathrm{V\ L2}]} \underbrace{-4\mathcal{A}(2)\mathcal{B}(1)A(1 2)\mathrm{TAB}}_{[\mathrm{V\ L3}]} \\ & + A(1\ 2)A(1\ 2)(\mathrm{TAB})^2 \quad \leftarrow [\mathrm{V\ L4}] . \end{aligned}$$

We will consider the reduction of the angular integrals. For dealing with most of the kinetic energy (II) terms, it is more convenient to work with the breakup of Eq. (6.22).

Note in the following review of II terms, we interchange orders of integration. It has been verified that this is proper.

(II.9) $\int \phi^*(1\ 2)\ H(1\ 2)\ \phi(1\ 2)\ d1\ d2$

$$\equiv \int \psi^*(1''2'')\ U^*(1''1)\ U^*(2''2)H(1\ 2)U(1\ 1')U(2\ 2')\psi(1'2')\ d1\ d2\ d1'\ d2'\ d1''\ d2''\ .$$

For the single particle part, i.e. H(1), we can use

(II.10) $$\int U^*(2''2)\ U(2\ 2')\ d2 = \delta(2''-2')\ ,$$

to simplify integration. Now in

(II.11) $$\int \psi^*(1''2'')\ U^*(1''1)\ H(1)\ U(1\ 1')\ \psi(1'2'')\ d1\ d1'\ d1''d2''$$

with $\psi(1\ 2) = N \exp \{-\frac{A}{2}(r_1^2+r_2^2) + B\bar{r}_1\cdot\bar{r}_2\}$, take $\int d2''$,

(II.12) $\int \psi^*(1''2'')\ \psi(1'2'')\ d2'' =$

$$= N^2(\tfrac{\pi}{A})^{3/2}\ e^{-\frac{1}{2}(A-\frac{B^2}{2A})(r_{1''}^2+r_{1''}^2)+\frac{B^2}{2A}\bar{r}_{1''}\cdot\bar{r}_{1'}}\ .$$

(II.13) $$U\,H\,U = \delta\,H\,\delta - \delta\,H\,A - A\,H\,\delta + A\,H\,A\ .$$

Consider the last three terms a', b', c'.

Take d1"

$$(a') = -N^2\left(\frac{\pi}{A}\right)^{3/2}\int e^{-\frac{1}{2}\left(A-\frac{B^2}{2A}\right)\left(r_1^2+r_{1'}^2\right)+\frac{B^2}{2A}\bar{r}_1\cdot\bar{r}_{1'}}$$

$$\cdot\ H(1)\ A(1\ 1')\ d1\ d1'\ .$$

(Note H act on quantities to the right only.)

$$(b') = -\ N^2\left(\frac{\pi}{A}\right)^{3/2}\int A(1''1)\ H(1)$$

$$\cdot\ e^{-\frac{1}{2}\left(A-\frac{B^2}{2A}\right)\left(r_{1''}^2+r_1^2\right)+\frac{B^2}{2A}\bar{r}_{1''}\cdot r_1}\ d1\ d1''\ ;$$

$$(c') = +\ N^2\left(\frac{\pi}{A}\right)^{3/2}\int A(1''1')\ e^{-\frac{1}{2}\left(A-\frac{B^2}{2A}\right)\left(r_{1''}^2+r_{1'}^2\right)+\frac{B^2}{2A}\bar{r}_{1''}\cdot\bar{r}_{1'}}$$

$$\cdot\ d1''\ d1'\int\mathcal{A}(1)H(1)\mathcal{A}(1)\ d1\ .$$

Use

$$(\text{II.14})\quad \nabla_1^2\ e^{-\alpha r_1^2+\beta\bar{r}_1\cdot\bar{r}_2} = \left\{-6\alpha+4\alpha^2r_1^2+\beta^2r_2^2-4\alpha\beta\bar{r}_1\cdot\bar{r}_2\right\}$$

$$\cdot\ e^{-\alpha r_1^2+\beta\bar{r}_1\cdot\bar{r}_2}$$

$$(\text{II.15})\quad \sqrt{1-(uv)}\ \nabla_1^2\mathcal{A}(1) = \left(\frac{\alpha}{\pi}\right)^{3/4}\left(\alpha^2r_1^2-3\alpha\right)e^{-\frac{\alpha}{2}r_1^2}$$

$$+\left(\frac{b^3}{\pi}\right)^{1/2}\left(\frac{2b}{r_1}-b^2\right)e^{-br}\ .$$

Note the δHδ contribution coincides with Eq. (6.16), which has been calculated previously and is our entire I term. We now define a number of quantities and present some integrals to be used in reducing the order of the II integral.

Let

$$\text{(II.16)} \qquad \mathrm{EXB} = e^{-\frac{1}{2} A(r_1^2+r_2^2)+ \frac{B^2}{4A}(r_1+r_2)^2}$$

$$\text{(II.17)} \qquad \mathrm{EXM} = e^{-\frac{1}{2} A(r_1^2+r_2^2)+ \frac{B^2}{4A}(r_1-r_2)^2}$$

$$\text{(II.18)} \qquad \mathrm{DLA} = r_1 \nabla_1^2 \ \bar{\mathcal{A}}\ (1)$$

$$\text{(II.19)} \qquad - \overline{\mathrm{TCB}} = \bar{H} = \int \bar{\mathcal{A}}\ (1)\ H(1)\ \bar{\mathcal{A}}\ (1)\ d1$$

$$= \frac{1}{\pi} \int [-2 \ \bar{\mathcal{A}}\,(1)\ r_1\ \overline{\mathrm{DLA}} - 8r_1 \ \bar{\mathcal{A}}^2(1)].$$

The resulting sum of the II terms a,b c, is

$$\text{(II.20)} \qquad \frac{32\ \bar{N}^2}{\pi B^2 \sqrt{\pi A}} \int \bar{\mathcal{A}}\ (2)\ r_2 \Big\{ (\mathrm{EXB}-\mathrm{EXM})(0.5 * \overline{\mathrm{DLA}} + \bar{\mathcal{A}}\ (1)$$

$$\cdot\ [4.-r_1(\overline{\mathrm{TCB}}-0.5 * A + \frac{B^2}{4A}) + 0.5(A^2-B^2+ \frac{B^4}{4A^2})r_1^3$$

$$+ \frac{B^4}{8A^2}\ r_2^2 r_1]) - (0.5\ B^2 - \frac{B^4}{4A^2}) r_1^2 r_2 (\mathrm{EXB} + \mathrm{EXM}) \Big\} dr_1\ dr_2$$

For B = 0 limit

$$\text{(II.21)} \qquad \frac{\mathrm{EXB} - \mathrm{EXM}}{B^2} = e^{-\frac{1}{2} A(r_1^2 + r_2^2)} * \frac{r_1 r_2}{A}\ .$$

(Note the above results are in my "bar" notation where $\bar{N}^2 = \pi^3 N^2$. $\bar{\mathcal{A}} = \pi \mathcal{A}$, $\overline{\mathrm{DLA}} = \pi$ DLA. These definitions can used to convert to ordinary notation.)

The following equations have been used:

$$\text{(II.22)} \qquad \int e^{\beta \bar{r}_1 \cdot \bar{r}_2} \, d\Omega_1 \, d\Omega_2 = \frac{(4\pi)^2 \sinh \beta \, r_1 r_2}{\beta \, r_1 \, r_2}$$

$$\text{(II.23)} \qquad \int \bar{r}_1 \cdot \bar{r}_2 \, e^{\beta \bar{r}_1 \cdot \bar{r}_2} \, d\Omega_1 \, d\Omega_2 = \frac{d}{d\beta} \cdot \text{(II.22)}$$

$$= - \left(\frac{4\pi}{\beta}\right)^2 \frac{\sinh \beta \, r_1 r_2}{r_1 r_2} + \frac{(4\pi)^2}{\beta} \cosh \beta \, r_1 r_2$$

$$\text{(II.24)} \qquad \int_0^\infty x \, e^{-Ax^2} \sinh x R \, dx = \frac{1}{4A} \sqrt{\frac{\pi}{A}} \, R \, e^{R^2/4A}$$

$$\text{(II.25)} \qquad \int_0^\infty e^{-Ar_2^2} \, r_2^2 \, d^2 r_2 \int_r \bar{r}_1 \cdot \bar{r}_2 \, e^{B\bar{r}_2 \cdot \bar{r}_{1'} + C\bar{r}_2 \cdot \bar{r}_1} \, d\Omega_2$$

$$= \int_0^\infty e^{-Ar_2^2} \, r_2^2 \, dr_2 \, \frac{\partial}{\partial C} \int_r e^{r_2 R \hat{e}_2 \cdot \hat{e}_R} \, d\Omega_{2'} \; ,$$

with $R = |B\bar{r}_{1'} + C\bar{r}_1| = \sqrt{(B\bar{r}_1 + C\bar{r}_1) \cdot (B\bar{r}_{1'} + C\bar{r}_1)}$ ; we can apply (II.22) and assume $dr_2$ integration can be carried out before taking

$$\text{(II.26)} \qquad \frac{\partial}{\partial C} \left(\frac{\pi}{A}\right)^{3/2} e^{-\frac{R^2}{4A}} = \left(\frac{\pi}{A}\right)^{3/2} \frac{2(C\, r_1^2 + B\, \bar{r}_1 \cdot \bar{r}_{1'})}{4A}$$

$$\cdot \; e^{(B\bar{r}_{1'} + C\bar{r}_1) \cdot (B\bar{r}_{1'} + C\bar{r}_1)/4A} \, .$$

(II.27) $$\int_0^\infty e^{-Ar_2^2} r_2^4 \, dr_2 \int_r e^{Br_2 \hat{e}_2 \cdot \hat{e}} \, d\Omega_2 =$$

$$= - \frac{\partial}{\partial A} [ (\frac{\pi}{A})^{3/2} e^{B^2/4A} ]$$

$$= e^{B^2/4A} [ \frac{3}{2A} (\frac{\pi}{A})^{3/2} + \frac{B^2}{4A^2} (\frac{\pi}{A})^{3/2} ]$$

Note for B = C in (II.26), let B = C in result and get

$$(\frac{\pi}{A})^{3/2} \frac{B}{2 \ A} (r_1^2 + \bar{r}_1 \cdot \bar{r}_{1'}) \ e^{\frac{B^2}{4A}(r_1^2 + r_{1'}^2 + 2\bar{r}_1 \cdot \bar{r}_{1'})} .$$

Our II terms now give

$$\mathrm{IIa} = - 2 \int \psi^*(1 \ 2') \mathcal{A}(1') \ H(1) \mathcal{A}(1) \ \psi(1'2') \ d1 \ d1' \ d2' .$$

$$= - \frac{32}{\pi^{3/2}} \frac{\bar{N}^2}{\sqrt{A} \ B^2} \int (\mathrm{EXB} - \mathrm{EXM}) r_1 r_{1'} \ \bar{\mathcal{A}} (1') \ H(1) \bar{\mathcal{A}}(1) \ dr_1 dr_{1'}$$

$$= + \frac{32}{\pi^{3/2}} \frac{\bar{N}^2}{\sqrt{A} \ B^2} \int (\mathrm{EXB} - \mathrm{EXM}) r_{1'} \ \bar{\mathcal{A}} (1') \cdot$$

$$\cdot [ \frac{1}{2} r_1 \nabla_1^2 + 2 ] \ \bar{\mathcal{A}} (1) \ dr_1 \ dr_{1'} \ .$$

$$\mathrm{IIb} = - 2 \int \psi^*(1'2') \ A(1'1) \ H(1) \ \psi(1 \ 2') \ d1 \ d1' \ d2'$$

$$= + \frac{32}{\pi^{3/2}} \frac{\bar{N}^2}{\sqrt{A} \ B^2} \cdot 2 \int \bar{A}(1'1) r_1 r_2 \ e^{- \frac{1}{2}(A - \frac{B^2}{2A})(r_1^2 + r_{1'}^2)} .$$

$$\cdot\ \Big[\sinh \frac{B^2}{2A} r_1 r_{1'} \left\{\frac{2}{r_1} - \frac{A}{2} + \frac{B^2}{4A} + \frac{1}{2}\Big(A^2 - B^2 + \frac{B^4}{4A^2}\Big) r_1^2 + \frac{B^4}{8A^2} r_{1'}^2\right\}$$

$$- r_1 r_{1'} \Big(\frac{B^2}{2} - \frac{B^4}{4A^2}\Big) \cosh \frac{B^2}{2A} r_1 r_{1'}\Big]\, dr_1\, dr_{1'}$$

$$\text{IIc} = + 2\, \bar{H} \int \psi^*(1'2')\, A(1\ 1')\, \psi(1\ 2')\, d1\, d1'\, d2'$$

$$= + \frac{32}{\pi^{3/2}} \frac{\bar{N}^2}{\sqrt{A}\ B^2} \int (\text{EXB} - \text{EXM})\, r_1 r_1'\ \bar{\mathcal{A}}\,(1\ 1')\, dr_1\, dr_{1'} \cdot \bar{H}.$$

We now must evaluate $\mathcal{B}(1) = \int \mathcal{A}(2)\psi(1\ 2)\, d2$, which is used in the reduction of the $1/r_{12}$ terms. Using our table of integrals, we get

$$\text{(II.28)}\quad \mathcal{B}(2) = N \frac{e^{-\frac{A}{2} r_2^2}}{\sqrt{1 - \int v_0 u_0\, d2'}} \int e^{-\frac{A}{2} r_1^2 + B\bar{r}_1 \cdot \bar{r}_2}$$

$$\cdot \left\{\Big(\frac{\alpha}{\pi}\Big)^{3/4} e^{-\frac{\alpha}{2} r_1^2} - \sqrt{\frac{b^3}{\pi}}\, e^{-br_1}\right\} d1\ ;$$

$$\text{(II.29)}\quad \int e^{B\bar{r}_1 \cdot \bar{r}_2}\, d1 = \frac{4\pi}{Br_1 r_2} \sinh\, (Br_1 r_2)\ ;$$

$$\text{(II.30)}\quad \mathcal{B}(2) = \frac{N\ e^{-\frac{A}{2} r_2^2}}{\sqrt{1 - \int v_0 u_0\, d2'}} \left\{\Big(\frac{\alpha}{\pi}\Big)^{3/4} \Big(\frac{2\pi}{A+\alpha}\Big)^{3/2}\right.$$

$$\cdot\ e^{B^2 r_2^2/2(\alpha+A)} - \frac{1}{2} \Big(\frac{2\pi}{A}\Big)^{3/2} \sqrt{\frac{b^3}{\pi}}\ \frac{1}{Br_2}\ [(b+Br_2)\cdot$$

$$\cdot\ e^{(b+Br_2)^2/2A} \quad \mathrm{erfc}\ \left(\frac{b+Br_2}{\sqrt{2A}}\right) - (b-Br_2)\, e^{(b-Br_2)^2/2A}$$

$$\left.\cdot\ \mathrm{erfc}\ \left(\frac{b-Br_2}{\sqrt{2A}}\right)\right]\Bigg\} .$$

The complementary error function is denoted by erfc(x). Let $\mathcal{S}(BR) = \frac{1}{Br}\ [\ldots]$. At $Br = 0$, we must take a Taylor expansion or do the integration for this point specifically. The result obtained either way is

$$\mathcal{S}(0) = 2\ \left[\left(1 + \frac{b^2}{A}\right)\ e^{b^2/2A} \quad \mathrm{erfc}\left(\frac{b}{\sqrt{2A}}\right) - \sqrt{\frac{2}{\pi A}}\ b\right] .$$

Note in the $B = 0$ limit when $\psi(1\ 2) = u_0(1)u_0(2)$, using $\mathcal{S}(0)$, and rearranging constants, this does reduce to the proper limit of $\mathcal{B}(2) = u_0(2)\sqrt{1 - \int v_0 u_0\ d2'}$ .

We now can give a review of the reduced form of the rest of the integrals that were used.

$$\int \psi^*(1\ 2) \quad (2)\ \frac{1}{r_{1\,2}}\ \mathcal{B}(1)\ d1\ d2 \qquad \text{III-4}$$

$$2\int \quad (1)\ A(2\ 2)/r_{1\,2}\ \mathcal{B}(1)\ d1\ d2 \qquad \text{IV}$$

$$2\int \psi^*(1\ 2)\ A(1\ 2)/r_{1\,2}\,\mathrm{TAB}\ d1\ d2\ ,$$

$$\mathrm{TAB} = \int A(1'2')\psi(1'2)\ d1'd2 \qquad \text{V L1}$$

$$2\int \mathcal{B}(1)\ A(1\ 2)/r_{1\,2}\ \mathcal{B}(2)\ d1\ d2 \qquad \text{V L2}$$

$$- 4 \int \mathcal{B}(1) \mathcal{A}(1)\, A(2\ 2)/r_{1\,2}\, TAB\ d1\ d2 \qquad \text{V L3}$$

$$(TAB)^2 \int \frac{A(1\,1)\, A(2\,2)}{r_{1\,2}}\, d1\ d2 \qquad \text{V L4}$$

For further reduction, use

$$\text{(II.31)} \qquad \int \frac{d\Omega_1\ d\Omega_2}{r_{1\,2}} = \frac{8\pi^2}{r_1 r_2} (r_1+r_2-|r_1-r_2|) \ ;$$

$$\text{(II.32)} \quad \int \psi^*(1\ 2)/r_{1\,2}\ d\Omega_1\ d\Omega_2 = 4\pi\ N\ e^{-\frac{A}{2}(r_1^2+r_2^2)} \cdot$$

$$\cdot \frac{\pi^{3/2}}{r_1 r_2} \left(\frac{2}{B}\right)^{1/2} \left[ \Phi\left(\sqrt{\tfrac{B}{2}}\ [r_1+r_2]\right) - \Phi\left(\sqrt{\tfrac{B}{2}}\ |r_1-r_2|\right)\right]$$

$$\cdot\ e^{\frac{B}{2}(r_1^2+r_2^2)} \ .$$

For B small or for negative B, we replace

$$\sqrt{\frac{2}{B}}\ \left[\ \Phi\left(\sqrt{\tfrac{B}{2}}\ |r_1+r_2|\right) - \Phi\left(\sqrt{\tfrac{B}{2}}\ |r_1-r_2|\right)\right] ,$$

where $\Phi$ is the error function by

$$\frac{2}{\sqrt{\pi}} \sum_{0}^{\infty} \frac{(-B)^n[(r_1+r_2)^{2n+1} - |r_1-r_2|^{2n+1}]}{2^n\ n!(2n+1)} \ .$$

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